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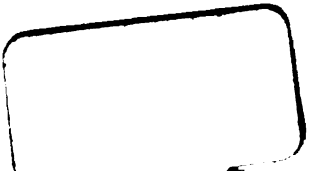


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ON TRIVALENT CARBON.

(FOURTH PAPER.)

BY M. GOMBERG.

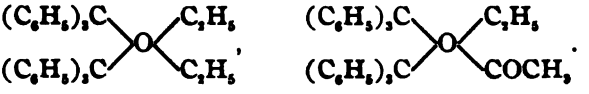
Received April 9, 1902.

IT was shown in previous papers upon this subject that by the action of various metals upon triphenylchlormethane an extremely unsaturated hydrocarbon is produced, to which was assigned the constitution of triphenylmethyl, $(C_6H_5)_3C$. The hydrocarbon was found to unite very readily not only with atmospheric oxygen and with iodine, but also with a number of oxygen compounds, such as ethyl ether, acetic ester, etc. The simple oxygen compound was shown to possess the constitution of a peroxide, being formed by the direct addition of a molecule of oxygen to the unsaturated hydrocarbon:

$$\begin{matrix}(C_6H_5)_3C \\ (C_6H_5)_3C\end{matrix} \quad \begin{matrix}O \\ \| \\ O\end{matrix} \quad = \quad \begin{matrix}(C_6H_5)_3C-O \\ | \\ (C_6H_5)_3C-O\end{matrix}.$$

This peroxide is a beautifully crystalline stable body, only very slightly soluble in the usual organic solvents, and shows none of the unsaturated properties of the original hydrocarbon. The ether and ester compounds, on the contrary, still possess the unsatura-

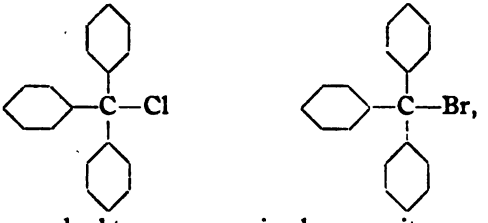
tion to the same extent as the hydrocarbon itself. Their solutions, when exposed to air, absorb oxygen almost as readily as triphenylmethyl itself, and also give the above-mentioned peroxide. The composition of these compounds was found to be 2 molecules of triphenylmethyl to 1 molecule of the ether or the ester. The theory was tentatively advanced[1] that the constitution of these bodies could best be explained by assuming the existence of tetravalent oxygen:



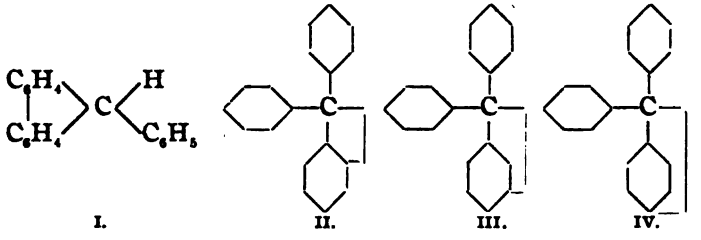
Experiments have since shown that this reaction of the hydrocarbon towards ethers and esters is quite general. Analogous compounds are formed with methylpropyl ether, ethylpropyl ether, methylbenzyl ether; with methyl acetate and other esters. Experimental data in favor of the existence of tetravalent oxygen were, at the time when the above formulas were proposed, very few. The principal support in favor of such a view was to be found in the physico-chemical studies of Brühl,[2] in the work of Collie and Tickle[3] upon the oxonium bases of dimethylpyron, and in the azoxonium bodies of Kehrmann.[4] Since the publication of my last paper, several important contributions in regard to the existence of tetravalent oxygen have been published. We should be quite justified at present, in the light of the recent work of Baeyer and Villiger,[5] Werner,[6] Walden,[7] Büllow and Sicherer,[8] and Kehrmann[9] to consider the existence of tetravalent oxygen as entirely probable, and to employ this probability as a support of the view as to the constitution of the ether and ester compounds of triphenylmethyl. Still, even at present, it seems best to adhere to the original plan: to place the constitution of triphenylmethyl itself upon an experimental basis first; after that we can employ this extremely unsaturated body for a further study of the valency of oxygen, and perhaps that of other elements.

[1] This Journal, 23, 501.
[2] *Ber. d. chem. Ges.*, 28, 2847, etc.
[3] *J. Chem. Soc.*, 75, 710.
[4] *Ber. d. chem. Ges.*, 32, 2610; 34, 1623.
[5] *Ibid.*, 34, 2679, 3612.
[6] *Ibid.*, 34, 3300.
[7] *Ibid.*, 34, 4185.
[8] *Ibid.*, 34, 3916.
[9] *Ibid.*, 35, 341, 343.

That the constitution of triphenylchlormethane and triphenylbrommethane is really as shown below,



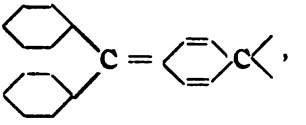
there can be no doubt, as was again shown quite recently by Kehrmann.[1] It is well known that metals may act upon halogen compounds in either of the two ways: (1) the halogen alone may be removed, and then 2 radicals unite into 1 molecule; (2) the metal may induce the splitting off of a halogen acid, and thus give rise to an unsaturated body. If metals affect triphenylchlormethane in such a way as to cause the removal of hydrochloric acid then the constitution of the resulting body may be expressed by one of the following four formulas:



I. II. III. IV.

A substance possessing constitution I has been prepared some time ago by Hemilian,[2] and also by E. and O. Fischer,[3] by the action of heat (250° C.) upon triphenylchlormethane. It is a stable, saturated hydrocarbon, and is different in every respect from the "triphenylmethyl" described by myself. Formulas II, III, and IV[4] give no adequate explanation why the hydrocarbon should be so very unstable and unsaturated. Because of these considerations I expressed myself as follows[5]: "Should it be proved at some future time that the action of metals upon triphenylchlormethane results, after all, in the elimination of hydrochloric acid, the behavior of the hydrocarbon will best be explained by the constitution

[1] *Ber. d. chem. Ges.*, 34, 3818.
[2] *Ibid.*, 7, 1208.
[3] *Ann. Chem.* (Liebig), 194, 259.
[4] Norris: *Am. Chem. J.*, 28, 122.
[5] *Am. Chem. J.*, 28, 333.



involving the existence of bivalent carbon". Kehrmann,[1] in a recent paper, seems to give preference to this constitution, without, however, advancing any new experimental proofs.

It has, however, been assumed by me all along that metals in this instance do not split off hydrochloric acid, but only the chlorine, giving as a result the free radical, triphenylmethyl, $(C_6H_5)_3C$. One of the reasons for this assumption was the fact that by the action of iodine upon the unsaturated hydrocarbon a body of the composition $(C_6H_5)_3CI$ was obtained. As the yield was very small, only a few qualitative tests were made, and little could be said with certainty as to the mechanism of its formation. The reaction has now been studied in detail, and it will be shown that if certain conditions are observed it is possible to obtain triphenyliodomethane almost *quantitatively*. The iodocompound is an extremely unstable body, and the isolation of it in the dry state is attended with great difficulties. It was therefore prepared in most instances only in solution in some organic solvent, and the solution was at once used up for the experiments. I have made a comparative study of the reactions of triphenylchlormethane and triphenylbrommethane on one hand, and triphenyliodomethane on the other, with the result that the latter was found to be absolutely identical in its chemical behavior with the former two. The following reactions were studied: 1. Amount of iodine taken up by the hydrocarbon; 2. Reaction of the iodocompound with ammonia; 3. Reaction with substituted amines; 4. Formation of perhalides; 5. Empirical composition of the iodocompound; 6. Formation of double salts with the halide salts of metals.

I. TITRATION WITH IODINE.

Preparation of the Hydrocarbon.—The triphenylmethyl was prepared in the following way: 20 grams of triphenylchlormethane are dissolved in thoroughly dried benzene, and about 10 grams of zinc in the form of turnings or sticks are added to the solution. All the air in the flask must be completely displaced by

[1] *Ber. d. chem. Ges.*, 34, 3815.

dry carbon dioxide. The solution at once turns yellow, and the metal soon becomes coated with a number of small droplets of a dark viscous mass. This syrupy material is a compound, in the nature of a double salt, of triphenylchlormethane with the zinc chloride which has been formed in the reaction. In five to fifteen days, depending upon the amount of the surface of zinc exposed, the reaction is completed. About 15 grams of the chlorocompound are reduced to the triphenylmethyl, while about 5 grams combine with the zinc chloride, forming a compound which is insoluble in benzene and which is therefore no further attacked by the metal. The benzene solution of triphenylmethyl is siphoned off from the zinc and the precipitated double salt, and is concentrated to a small bulk under diminished pressure. All the air must be rigorously excluded throughout the whole operation. If now to the very concentrated benzene solution acetic ester be added the ester compound will separate in a very short time in transparent, colorless crystals. By the addition of ethyl ether instead of the ester, the corresponding ether combination may be similarly obtained. If, however, acetone is added then one of the following two things will happen: If the solution still contains about 15 cc. of benzene then the triphenylmethyl will separate in combination with benzene, although the latter has become diluted with a large quantity of acetone; but if care has been taken to drive off all, or nearly all, the benzene before the acetone is added then the pure triphenylmethyl is obtained as a colorless, granulated precipitate. This tendency on the part of the hydrocarbon to enter into combination with benzene has been noticed in other instances, when solvents other than acetone are added to a concentrated benzene solution of the triphenylmethyl. It is peculiar that the combination of the hydrocarbon with benzene is in the same proportions as in the case of the ether and ester compounds: 2 molecules of the triphenylmethyl to 1 of the solvent.

A sample of the benzene compound obtained by the addition of acetone as described above, furnished on analysis the following results:

0.379 gram substance gave 1.2930 gram CO_2 and 0.2250 gram H_2O.

	Calculated for $2(C_6H_5)_3C + C_6H_6$.	Found.
Carbon	93.56	93.00
Hydrogen	6.44	6.59

A portion, 1.622 grams, was heated for some time in a stream of carbon dioxide at 80°-90° C., and the loss amounted to 0.2100 gram.

	Calculated for $2(C_6H_5)_3C + C_6H_6$.	Found.
Loss, as benzene....	13.83	12.94

The escaping vapors were condensed in a freezing-mixture and were identified as benzene by the melting-point, the characteristic odor, and the smoky flame. In another instance, a combustion of the condensed liquid was made and the results proved beyond doubt that it was benzene.

For the preparation of the pure triphenylmethyl in all subsequent work the benzene solution of the hydrocarbon was evaporated to dryness and the dry crystalline residue was heated for an hour in a vacuum at 60°-80° C. To the residue warm acetone was added and the mixture was kept at a temperature of boiling acetone for one-half hour. On cooling, the crystalline mass was filtered, washed several times with acetone, and dried in a stream of carbon dioxide.

1.4600 grams were heated for two hours at 80° C., then for three hours at 90° C., and the loss amounted only to 0.0005 gram.

0.3307 gram substance gave 1.1310 gram CO_2 and 0.1851 gram H_2O.

	Calculated for $(C_6H_5)_3C$.	Found.
Carbon	93.74	93.28
Hydrogen.....	6.26	6.22

Triphenylmethyl when dry is a fairly stable substance. It may be exposed to air for a short time without danger of oxidation. It is white when freshly prepared, but soon turns pale yellow. It is soluble in benzene, carbon disulphide, only slightly soluble in acetone, and hardly at all in petroleum ether. While colorless itself, the solutions of triphenylmethyl are always yellow, no matter what solvent be employed. This phenomenon will be studied more fully later. The solutions of the hydrocarbon when exposed to air instantly become covered on the surface with a crystalline crust of the peroxide; in a short time the whole of the triphenylmethyl is converted into the oxidized product, and the supernatant liquid becomes colorless.

Titration.—Triphenylmethyl absorbs not only oxygen but also iodine. When a solution of the latter is added to that of the

former the iodine is absorbed instantly, the solution remaining pale yellow till nearly the end of the reaction. Many attempts have been made to make this a basis of a quantitative method for the estimation of the hydrocarbon, but owing to the instability of the triphenyliodomethane, only approximately quantitative results could be obtained. It will be seen from the reaction,

$$(C_6H_5)_3C + I = (C_6H_5)_3CI,$$

that the hydrocarbon requires 52.17 per cent. of its own weight of iodine for complete saturation. Similarly, when the acetic ester or the benzene compound are used for the titration it ought to proceed according to the equations

$$[(C_6H_5)_3C]_2.CH_3CO_2C_2H_5 + 2I = 2(C_6H_5)_3CI + CH_3CO_2C_2H_5,$$

$$[(C_6H_5)_3C]_2.C_6H_6 + 2I = 2(C_6H_5)_3CI + C_6H_6.$$

Accordingly, the ester compound should take up 44.2 per cent., and the benzene derivative 45 per cent. of iodine respectively for their complete saturation. The method of procedure was as follows: The substance to be titrated was placed in a flask from which all the air had been displaced by carbon dioxide. The substance was then either dissolved or just covered with a solvent, such as benzene, carbon disulphide, or petroleum ether, and a standard solution of iodine, from tenth-normal to half-normal, also in one of the above-mentioned solvents, was gradually added to the hydrocarbon. At the beginning, the halogen is taken up at once, the solution remaining pale yellow. After about 75-80 per cent. of the theoretical amount of the halogen has been added the absorption becomes noticeably slower and the solution grows darker in color; any further addition of halogen above 80-85 per cent. only tends to deepen the color. A large number of experiments were made in order to determine the cause why the reaction does not proceed smoothly to the end. Of the several explanations which have been thought of in this connection the following may be mentioned here as appearing, for the present, the most plausible: The triphenyliodomethane which is formed during titration is an exceedingly unstable body; when in solution it rapidly breaks down, being quite readily affected by light, and completely decomposed by atmospheric oxygen. When, in titration, about four-fifths of the triphenylmethyl is converted into the halogen derivative an equilibrium is apparently established; beyond this point any further

formation of the iodocompound will be checked by a corresponding decomposition with liberation of iodine.

The study of this halogen compound involves a great many difficulties, and anything like quantitative results can only be obtained by observing the strictest precautions, especially in regard to the exclusion of oxygen from the apparatus. In the following table is given a summary of the results obtained in this part of the work. The amounts of iodine indicated are those added until the pale yellow solution of the hydrocarbon just began to turn darker in color.

Substance employed.	Solvent.	Amount of substance. Grams.	Quantity of iodine taken up. Grams.	Per cent. of iodine taken up.	Per cent. of iodine required by theory.	Per cent. absorbed as compared with the theoretical amount.
Acetic ester compound	Benzene	5.1200	1.8132	35.41	44.20	80.10
Acetic ester compound	Benzene	2.9500	0.9967	33.78	44.20	76.50
Acetic ester compound	Benzene	2.8500	1.0014	35.21	44.20	80.00
Benzene compound	Benzene	1.3640	0.4760	34.17	45.00	77.50
Benzene compound	Carbon disulphide	2.0900	0.8252	39.00	45.00	86.70
Triphenylmethyl	Benzene	1.7380	0.6955	40.00	52.17	76.70
Triphenylmethyl	Benzene	2.0540	0.8620	42.00	52.17	80.40
Triphenylmethyl	Benzene	1.5150	0.6275	41.41	52.17	79.40
Triphenylmethyl	Carbon disulphide	1.5650	0.6874	43.92	52.17	84.10
Triphenylmethyl	Carbon disulphide	1.7060	0.7375	42.65	52.17	81.70

The table clearly shows that under the conditions above described about four-fifths, or somewhat more, of the hydrocarbon can be titrated without difficulty. All the solutions of the triphenyliodomethane obtained as given in the above table were at once used up for further experiments to be described below. In nearly every instance there was obtained some peroxide, which points to an incomplete saturation in the titration. Results considerably nearer to quantitative were obtained later in the work,

in the preparation of triphenyliodomethane in the dry state. The triphenylmethyl was covered with petroleum ether and warmed on the water-bath. To the warm mixture a standard solution of iodine in the same solvent was slowly added. The titration has to be carried on slowly, so as to prevent the separation of the triphenyliodomethane through the addition of the cold iodine solution. The end-reaction can be recognized fairly well. 2.3700 grams of triphenylmethyl took up 1.0342 grams iodine, which represents 83.60 per cent. of the theoretical amount. In working up this solution for triphenyliodomethane there was also separated nearly 0.300 gram of a mixture of the peroxide and some other body. By deducting this from the original 2.3700 grams, we see that the amount of absorbed iodine would be equivalent to 96 per cent. of the amount required by theory. In another instance, 2.4900 grams required 1.0710 grams iodine, or 82.4 per cent. of the theoretical amount. By subtracting 0.350 gram of non-halogen product found on working up the reaction mixture, we find that the amount of iodine actually taken up represents again almost 96 per cent. of the amount required by theory for pure triphenylmethyl. Further study of this question is necessary.

2. REACTION WITH AMMONIA.

It was shown by Elbs,[1] and by Hemilian and Silberstein,[2] that triphenylbrommethane reacts with ammonia and gives triphenylamine. The same reaction was carried out by Nauen[3] on triphenylchlormethane. I find that triphenyliodomethane reacts at *ordinary* temperature with ammonia, and the yield of the amine compound is almost quantitative.

4 grams of the acetic ester compound of triphenylmethyl were dissolved in benzene, and iodine added as described under titration. 1.4960 grams of the halogen were added. The solution was then placed in ice-water and dry ammonia was passed into the solution of the halogen compound. The separation of ammonium iodide began with the first few bubbles of the gas. The ammonium iodide was filtered off, the benzene solution concentrated to a small bulk, and to that alcohol was added. On cooling, the triphenylaminomethane crystallized almost pure, containing a small

[1] *Ber. d. chem. Ges.*, 17, 703.
[2] *Ibid.*, 17, 741.
[3] *Ibid.*, 17, 442.

amount (0.150 gram) of the triphenylmethyl peroxide. It melted at 102° C., and agreed in every respect with the amine obtained from triphenylchlormethane in a parallel experiment. The yield was 2.6 grams, which represents 85 per cent. of the quantity required by theory. The calculation of the theoretical quantity of this and of the other amines must be made, of course, not upon the basis of triphenylmethyl used in the experiment, but only upon the amount of iodine added, because this alone determines the amount of triphenyliodomethane which is available in the reaction. For analysis, the amine was recrystallized from dilute alcohol.

0.2090 gram substance gave 0.6762 gram carbon dioxide and 0.1186 gram water.

0.2825 gram substance gave 14.9 cc. nitrogen at 23.5° C. and 748 mm.

	Calculated for $(C_6H_5)_3C.NH_2$.	Found.
Carbon	87.97	88.24
Hydrogen	6.63	6.31
Nitrogen	5.41	5.71

In another experiment 2.09 grams of the benzene compound of triphenylmethyl took up 0.8252 gram iodine and gave 1.995 grams of the almost pure amine, while the calculated quantity should have been 2.005 grams. One recrystallization from ether sufficed to furnish an absolutely pure product.

For further identification of the amine, the hydrochloride of it was prepared, which, on boiling with water, was converted into triphenylcarbinol, just as is the amine obtained by Elbs from triphenylbrommethane. The platinum double salts of the two amines were compared and were also found to be identical. There can be no doubt that the reaction above described takes place quantitatively according to the equation

$$(C_6H_5)_3CI + 2NH_3 = (C_6H_5)_3CNH_2 + NH_4I.$$

3. REACTION WITH SUBSTITUTED AMINES.

Triphenylchlormethane and triphenylbrommethane[1] react not only with ammonia but also with substituted amines, and give the corresponding substituted triphenylaminomethanes. The iodo-compound obtained by the addition of iodine to the unsaturated hydrocarbon behaves in every way similarly. It gives the identical substituted amines. While the reaction takes place quite readily

[1] Elbs: *Loc. cit;* Hemilian: *Loc. cit.*

and with good yield, with all the amines tried, by far the best results were obtained with para-toluidine. In this latter case the product obtained is at once pure, and the yield is as nearly quantitative as could be desired.

Triphenylmethylethylamine, $(C_6H_5)_3C.NH(C_2H_5)$. — 2.850 grams of the acetic ester compound of the hydrocarbon absorbed 1.001 grams of iodine. To this solution a little more than the theoretical amount of ethylamine in benzene was added. The reaction took place at once. On concentrating the filtered benzene solution of the amino-compound the latter separated as an oil which did not solidify until after several days' standing in a vacuum desiccator. The amine was dissolved in absolute ether, and precipitated as the hydrochloride by means of dry hydrochloric acid gas. In order to obtain the free base the salt was finely broken up under dilute alcoholic ammonia, filtered, washed with dilute alcohol and with water, and dried. Obtained in this way it is a white granular powder. When dissolved in any solvent it shows a great tendency to separate as an oil, which begins to crystallize only after some standing, or on introducing a crystal of the substance into the solution. When purified in this way it gives a melting-point of 75°-77° C. It behaves in every way as the simple triphenylaminomethane. It forms salts which suffer partial hydrolysis when dissolved in water, and which on boiling are completely decomposed with formation of triphenylcarbinol.

0.2995 gram substance gave 14 cc. nitrogen at 19° C. and 745 mm.

	Calculated for $(C_6H_5)_3CNH(C_2H_5)$.	Found.
Nitrogen.....	4.91	5.34

A sample of the same ethylamine compound was also prepared from pure triphenylchlormethane, and this was found to be absolutely identical with the one obtained from the iodo-compound in all its reactions, as well as in the tendency to separate from solvents in the form of an oil.

In the formation of this amine the reaction therefore proceeds as follows:

$$(C_6H_5)_3CI + 2C_2H_5NH_2 =$$
$$(C_6H_5)_3CNH.C_2H_5 + C_2H_5NH_2.HI.$$

Triphenylmethylpropylamine, $(C_6H_5)_3C.NHC_3H_7$.—This body was prepared in a manner analogous to that which furnished the

ethylamine derivative. It, also, possesses the tendency to remain oily. After standing in a vacuum desiccator for some time the oil solidifies to a solid crust of crystals. These can be purified by spreading them out upon a porous plate and washing first with petroleum ether, then with a little alcohol. The substance melts at 70° C.

0.2230 gram substance gave 11.5 cc. N at 27° C. and 741 mm.

	Calculated for $(C_6H_5)_3CNHC_3H_7$.	Found.
Nitrogen.....	4.65	5.06

The hydrochloride is easily formed by passing dry hydrochloric acid gas into an ethereal solution of the base. On boiling the base or the salt with dilute hydrochloric acid it decomposes, and triphenylcarbinol is produced, a reaction which is common to all the amines of triphenylmethyl,

$$(C_6H_5)_3CNHC_3H_7 + H_2O = (C_6H_5)_3C.OH + NH_2C_3H_7.$$

Triphenylmethylamylamine, $(C_6H_5)_3C.NH(C_5H_{11})$. — Amylamine acts upon the iodine compound apparently somewhat slower than the other amines mentioned, and the reaction is best hastened by gentle heat. The substance was obtained as an oil, and all attempts to bring it to crystallization have failed. It was therefore analyzed in the form of its hydrochloride, which was prepared in the same way as the salts of the other bases here described. The oil itself was also analyzed and gave results which indicate that it was pure triphenylpropylamine.

0.2300 gram substance gave 9.1 cc. N at 25° C. and 740 mm.

	Calculated for $(C_6H_5)_3CNHC_5H_{11}$.	Found.
Nitrogen.....	4.20	4.29

The oil was boiled with dilute hydrochloric acid, and the triphenylcarbinol obtained was of such purity as to require no further treatment for analysis. It melted as obtained at 159° C. Consequently the oil was pure triphenylmethylamylamine.

Triphenylmethylaniline, $(C_6H_5)_3C.NH(C_6H_5)$.—The reaction with aniline is very smooth; the resulting amine is produced in almost quantitative yield and is easily obtained pure. The experiment was repeated several times, and in no case was there noticed the formation of any other products than that of the aniline base and of some triphenylmethyl peroxide. In several instances the amount of aniline hydriodide formed in the reaction was also

determined, and was found to correspond exactly to the quantity of iodine added in the formation of the triphenyliodomethane. The yield of the aniline base, as well as that of the aniline salt, leaves no doubt that all the iodine added to the triphenylmethyl is used up in the formation of triphenyliodomethane, and that the reaction with aniline proceeds strictly according to the equation

$$(C_6H_5)_3CI + 2C_6H_5NH_2 =$$
$$(C_6H_5)_3CNHC_6H_5 + C_6H_5NH_2.HI.$$

In one experiment there was formed 14.5 grams of the crude aniline base while the amount required by theory was 16 grams. The product was divided into several portions and each purified by recrystallization from different solvents. The resulting products were all found to be identical, all melting at the same temperatures, namely at 149°-150° C. As Elbs gives the melting-point for the aniline base which he obtained from the triphenylbrommethane as 146° C., and as Hemilian gives it as 144.5° C., I prepared a sample of triphenylmethylaniline from carefully purified triphenylchlormethane, and found that it melts at 149°-150° C.

In another experiment 12 grams of the acetic ester compound of triphenylmethyl absorbed 4.3 grams iodine, and gave 9 grams of the aniline body. The latter was dissolved in ether and filtered in order to remove the small amount of triphenylmethyl peroxide mixed with the aniline base. On the addition of alcohol to the concentrated ethereal solution the triphenylmethylaniline crystallized in snow-white little prisms, possessing a melting-point of 148° C. The yield was 6.5 grams.

0.4607 gram substance gave 1.5010 grams CO_2 and 0.2697 gram H_2O.

0.4395 gram substance gave 17 cc. N at 22° C. and 729 mm.

0.3115 gram substance gave 12.2 cc. N at 19° C. and 742 mm.

	Calculated for $(C_6H_5)_3C.NH.C_6H_5$.	Found. I.	II.
Carbon	89.53	89.98	
Hydrogen ...	6.26	6.40	
Nitrogen	4.18	4.25	4.27

The base obtained from the iodo-compound agreed in every respect with that made from the corresponding chlor- and brommethane. On treatment with amyl nitrite it gave the nitroso derivative which, when heated slowly, was found to melt at 156° C., as given by Elbs.[1]

1 *Ber. d. chem. Ges.*, 17, 704.

Hemilian and Silberstein[1] state that when a benzene solution of triphenylmethylaniline is treated with hydrochloric acid gas it is decomposed even by the first few bubbles according to the equation

$$(C_6H_5)_3CNHC_6H_5 + HCl = (C_6H_5)_3C.Cl + C_6H_5NH_2.$$

This is correct in so far as a benzene solution of the base is concerned. But, curiously enough, if the benzene is diluted with absolute ether, or better still, if ether alone is employed as a solvent, then there is hardly any decomposition,—the base separates quantitatively as the hydrochloride salt. By this means the base can be readily and completely freed from the accompanying non-basic impurities.

Triphenylmethyl-o-toluidine, $(C_6H_5)_3C.NHC_6H_4CH_3$.—On the addition of orthotoluidine to a freshly prepared solution of triphenyliodomethane the reaction takes place at once. The hydriodide of the toluidine separates readily in the form of fine silky needles. On the addition of alcohol to the concentrated benzene solution the base is precipitated as an oil, which, however, soon changes to a crystalline mass. The crystals are dissolved in chloroform and separated by filtration from a little insoluble triphenylmethyl peroxide. On the addition of alcohol to the concentrated chloroform solution the triphenylmethyltoluidine crystallizes out pure, the crystals melting at 140° C., while the absolutely pure substance should melt at 142° C. The yield is about 80 per cent. of the calculated quantity. In one experiment, the base was obtained in a very pure state by precipitating the original benzene solution by means of ether instead of with alcohol, the subsequent purification being the same as before,—from a mixture of chloroform and alcohol.

0.2318 gram substance gave 8.9 cc. at 16.5° C. and 745 mm.

	Calculated for $(C_6H_5)_3CNH(C_7H_7)$.	Found.
Nitrogen.....	4.01	4.22

The preparation of the salts of this base is accompanied with very great difficulties, as has already been noticed by Elbs. In this respect this body behaves differently from the aniline compound. Hydrochloric acid gas decomposes quantitatively not only a benzene solution, but also an ethereal solution of the toluidine body:

$$(C_6H_5)_3CNHC_7H_7 + HCl = (C_6H_5)_3C.Cl + C_7H_7NH_2$$

[1] *Ber. d. chem. Ges.*, 17, 747.

Triphenylmethylmetatoluidine, $(C_6H_5)_3C.NH(C_6H_4CH_3)$, is formed when metatoluidine is added to a solution of triphenyliodomethane. The reaction is, however, much slower than in the formation of the above-described amines. The purification of the base cannot be done without considerable loss of material, as it is quite soluble in the usual solvents.

Triphenylmethylparatoluidine, $(C_6H_5)_3C.NH(C_6H_4CH_3)$.—Of all the amino-compounds tried, paratoluidine furnished the most satisfactory results. The product is very easily obtained pure, and the yield is fully 90 per cent. of the theory.

5.12 grams of the acetic ester compound of triphenylmethyl required for apparent saturation 1.8132 grams of iodine. 5 grams of para-toluidine in benzene were added to the solution of the iodo-compound; the reaction took place at once, at ordinary temperature. The toluidine hydriodide was removed by filtration, washed with benzene, dried, and weighed. The quantity found was 3.2 grams, while the calculated amount should have been 3.35 grams. The benzene solution was concentrated under reduced pressure, and to the residue a mixture of alcohol and ether was added. As triphenylmethyl-*p*-toluidine is only sparingly soluble in either of those two solvents it crystallized out at once pure, leaving the excess of toluidine in solution. The yield of the base was 4.55 grams, while the quantity calculated from the amount of iodine added should have been 5.003 grams; the actual yield, therefore, of the pure product was 90 per cent. of the theory. In a second experiment, 4 grams of the toluidine base were obtained, against 4.4 grams as calculated, which is equivalent to 91 per cent. of the theory.

For analysis the substance can be recrystallized from ether, or from a mixture of chloroform and alcohol. By either method it can be obtained in beautiful large transparent crystals, melting, as given by Elbs, at 177°-178° C.

0.3138 gram substance gave 1.0329 gram CO_2 and 0.1898 gram H_2O.

0.4496 gram substance gave 15.6 cc. nitrogen at 25° C. and 735 mm.

0.4617 gram substance gave 18.6 cc. nitrogen at 26° C. and 716 mm.

	Calculated for $(C_6H_5)_3CNHC_7H_7$.	Found. I.	II.
Carbon	89.39	89.77	
Hydrogen	6.65	6.71	
Nitrogen	4.01	4.31	4.25

4. FORMATION OF PERHALIDES.

It was reported by me[1] some years ago that on the addition of iodine to a solution of triphenylbrommethane a periodide is formed. The body possessed the appearance and properties of the periodides of organic bases. The analyses led me to the conclusion at that time that the composition of the body was $(C_6H_5)_3CBr.I_4$. I also described[2] a perbromide, the composition of which was found to be $(C_6H_5)_3CBr.Br_5$. Nef[3] reported that he got a perbromide of a composition similar to the periodide. As no figures of analysis are given by him it was to be interpreted[4] that he had a tetrabromide, $(C_6H_5)_3CBr.Br_4$. In analyzing the periodide which was made from triphenyliodomethane it was found that it had the composition $(C_6H_5)_3CI.I_5$. I have, therefore, decided to go over the whole work on the perhalides of triphenylmethane. It may be now considered established that there is a strict uniformity in composition in all these substances—they are all pentahalides.

Triphenylbrommethane Pentabromide, $(C_6H_5)_3CBr.Br_5$.—Triphenylbrommethane is dissolved in as little chloroform as possible and the calculated quantity of bromine is added. On cooling, the perbromide separates in dark orange crystals. These are rapidly filtered off, dried on a porous plate in soda-lime desiccator, and are analyzed at once. The total bromine was estimated by Carius' method; the "perbromine" was estimated by suspending weighed amounts of the perhalide in a solution of potassium iodide in water, adding some chloroform, and titrating the iodine set free by the "perbromine". Several samples were analyzed.

0.5569 gram substance gave total 0.8935 gram AgBr.

0.2712 gram substance gave 0.1548 gram perbromine.

0.3121 gram substance gave 0.1761 gram perbromine.

	Calculated for $(C_6H_5)_3CBrBr_5$.	Found. I.	II.
Total bromide	66.42	67.23	
Perbromine	55.32	55.04	56.4

[1] This Journal, 20, 790.

[2] *Ibid.*, 20, 1776.

[3] *Ann. Chem.* (Liebig), 308, 304.

[4] Beilstein: Ergänzungsband II, 127.

The perbromide is very unstable, losing bromine very readily, even in a desiccator, the residue consisting of pure triphenylbrommethane. It can, however, be kept without decomposition for a considerable length of time in a tightly closed bottle.

Triphenylbrommethane Pentiodide, $(C_6H_5)_3CBr.I_5$.—This can be prepared by the addition of the calculated quantity of iodine dissolved in benzene to a solution of triphenylbrommethane. The periodide separates as an oil which in a few seconds becomes crystalline. The yield is usually from 75 to 80 per cent. of the calculated quantity. The periodide is much more stable than the corresponding perbromide. It can be kept in a desiccator for days without any appreciable loss of iodine. It is only slightly soluble in benzene and in carbon disulphide, is quite soluble in ether, probably with decomposition. All the iodine can be titrated with standard thiosulphate solution in water, the bromide being at the same time converted into the carbinol.

The total halogen was estimated by reducing the perhalide in ether by means of a dilute solution of sulphurous acid in water, making the solution slightly alkaline, and then boiling the mixture for one-half hour in order to insure the complete conversion of the bromide into the carbinol. The solution of the sodium iodide and bromide is filtered from the carbinol and the total halogen estimated with silver nitrate. A large number of samples of this body were prepared under slightly varying conditions, in order to ascertain positively its composition. The best results were obtained by adding a *warm* solution of iodine to a *warm* solution of the bromide. Either benzene or carbon disulphide may be used as a solvent.

I. Sample from benzene:
0.6930 gram substance gave 0.4523 gram iodine.
0.6085 gram substance gave 0.3975 gram iodine.
0.7895 gram substance gave 1.1015 grams AgBr+AgI.

II. Sample from carbon disulphide:
0.5000 gram substance gave 0.3312 gram iodine.
0.4210 gram substance gave 0.2739 gram iodine.
0.4455 gram substance gave 0.2917 gram iodine.
0.6550 gram substance gave 0.9125 gram AgBr+AgI.

	Calculated for $(C_6H_4)_3CBr.I_4$.	Found. I.		II.		
Iodine ...	66.25	65.25	65.43	66.20	65.05	65.48
Bromine .	8.41	7.90		7.85		

The periodide is of a dark blue iridescent color. It melts at 92° C. It is quite probable that triphenylbrommethane may also give rise to lower periodides. The one reported by me as the tetraiodide was described as having a melting-point of 121° C.; and I once came across a periodide, also at this time, which melted at 120° C.

That we have here a true periodide of triphenylbrommethane, and that iodine did not replace bromine, is proved by the following two facts: First, some of the periodide was heated at 70°-80° C. until all the iodine was driven off; the residue was recrystallized from petroleum ether, and the product was found to be pure triphenylbrommethane. Second, some of the periodide was dissolved in ether and the solution was shaken with molecular silver until the color of iodine had just disappeared; on concentrating the filtered ethereal solution and recrystallizing the residue, pure triphenylbrommethane was again obtained.

Triphenyliodomethane Pentiodide, $(C_6H_5)_3I.I_5$.—This periodide is formed just as readily, if not more so, as the one described above. Indeed, it is even liable to be formed to some extent when triphenylmethyl is being titrated with iodine, unless the latter is added slowly. The hydrocarbon, or the ester or ether derivative of it, is dissolved in benzene or in carbon disulphide, and a solution of iodine in the same solvent is added until the end-reaction of the titration is reached. The solution is now gently warmed and more iodine is slowly added, with constant stirring, until the whole of the calculated amount is introduced. The periodide separates in fine shining needles, dark blue in color, and cannot be told by its appearance from the periodide of triphenylbrommethane. It is filtered, washed with a little benzene, and dried in a vacuum desiccator. Unlike the hydrocarbon, or the normal triphenyliodomethane, the periodide is stable, and can be exposed to dry air without fear of oxidation. The yield of the pure product is from 75 to 80 per cent. of the calculated amount, one part of triphenylmethyl furnishing three times its weight of the periodide. It melts at 90° C.

The total halogen is estimated, according to the method described under the periodide of the triphenylbrommethane, by reducing with sulphurous acid and precipitating with silver nitrate. If the periodide is dissolved, or merely suspended in ether and titrated with a standard solution of sodium thiosulphate, it will be found that of the *six* atoms of iodine only *five* can be titrated. This fact is very important, because it definitely proves that of the several atoms of iodine present in the molecule there is *one* that has an entirely distinct function, and this function corresponds to that of the bromine in triphenylbrommethane. Here again the titration must therefore be represented by the following equations:

$$2(C_6H_5)_3CI.I_5 + 10Na_2S_2O_3 =$$
$$2(C_6H_5)_3CI + 10NaI + 5Na_2S_4O_6.$$
$$(C_6H_5)_3CI + H_2O = (C_6H_5)_3C.OH + HI.$$

A few of the many analyses made will be given here.

0.5470 gram substance gave 0.7655 gram AgI.
0.5450 gram substance gave 0.3592 gram iodine by titration.
0.8805 gram substance gave 0.5788 gram iodine by titration.
0.4855 gram substance gave 0.6755 gram AgI.
0.7340 gram substance gave 0.4754 gram iodine by titration.
0.7700 gram substance gave 1.0650 grams AgI.
0.5680 gram substance gave 0.3651 gram iodine by titration.

	Calculated for $(C_6H_5)_3CI_5$.	Found. I.		II.	
Total iodine.....	75.79	75.65		75.18	75.10
Titrated iodine....	63.36	65.91	65.74	64.77	64.40

The carbinol formed in the reduction was identified by the melting-point, crystalline form, and by elementary analysis as such. Estimations of the yield of the carbinol gave results very close to those required by the equation.

It will be noticed from the figures of analysis that in all instances the titrated iodine was a little too high. This was puzzling, especially in view of the fact that the total halogen was always a little too low. The cause of this discrepancy was finally discovered to lie in the disturbing influence of the ether which is added in the titration. When either of the periodides is titrated with thiosulphate there is produced, at the early stages of the titration, triphenylbrommethane or triphenyliodomethane, and these form a coating over the crystals of the periodide; the further

action of the thiosulphate is in this way hindered. For this reason ether or some other solvent was added to keep the reduction products in solution. Triphenylbrommethane is affected by cold water only slowly, while the iodide is rapidly hydrolyzed, giving rise to the triphenylcarbinol and hydriodic acid. It is a well-known fact that in presence of certain substances hydriodic acid is far more affected by light than when pure. Pinnow[1] recently showed that small quantities of quinine and acridine sulphate exert a very appreciable effect upon the rate of oxidation of hydriodic acid solutions in water on exposure to light. I find that ether, also, greatly accelerates the oxidation. 50 cc. of a 0.5 per cent. solution of hydriodic acid, to which 15 cc. of ether were added, were exposed to ordinary diffused daylight for five minutes; almost 15 mg. of iodine were liberated in that short time. It is due, no doubt, to this influence of the ether present during the titration that high results are obtained in the case of triphenyliodo-periodide, while in the titration of the periodide of the brom-compound, ether has but little effect, as the solution remains nearly neutral till the end of the operation. Other immiscible solvents, such as chloroform, carbon disulphide, etc., also exert a marked influence upon the rate of oxidation. It seems therefore quite probable that the cause of this influence lies in the greater solubility of the iodine in the organic solvent than in water. The equilibrium being thus disturbed, more hydriodic acid will be oxidized.

Reactions of the Two Periodides. (1) *With Water.*—In this respect the two periodides behave absolutely alike. It has already been mentioned that during titration with sodium thiosulphate the triphenylcarbinol is formed. The same result can be reached without the use of any reducing agent, simply by boiling the periodides with water. Reduction of the iodides with a dilute solution of sulphurous acid, as described under the estimation of the total halogen, gave especially good results, the carbinol in both instances being formed quantitatively, and requiring no further purification. The carbinol was identified by its characteristic crystalline form and its melting-point (161°-162° C.) as well as by elementary analysis. There can be no doubt that in so far as the reaction with water is concerned the two periodides show exactly the same behavior.

[1] Ber. d. chem. Ges., 34, 1588.

(2) *Reaction with Alcohols.*—When triphenylbrom- or triphenyliodoperiodide is boiled with alcohol, and the excess of the iodine liberated in the reaction is removed by means of a solution of potassium iodide in water, the residue is triphenylmethane.[1] This formation of the hydrocarbon is not a result of the action of alcohol alone, but is caused by the hydriodic acid resulting from the interaction of the iodine and alcohol. This was established first, by a blank experiment with hydriodic acid and triphenylbrommethane; and second, by the following experiment, formed on each of the two periodides separately: The periodide was suspended in absolute alcohol, and to the solution small amounts of zinc dust were added, with constant stirring, until all the iodine was taken up by the zinc and the solution became clear. Water was now added, and the precipitated carbinol ether was freed from the alcohol and zinc iodide by filtration, and dried. The residue was recrystallized from ether and was identified as absolutely pure ethyl ether of triphenylcarbinol, $(C_6H_5)_3COC_2H_5$. No other products but the one mentioned were found. That the function of the zinc is no other than that of removing the "periodine" is quite evident from the fact that equally good results were obtained by substituting molecular silver for zinc. The action of alcohol upon the two periodides is therefore the same:

$$(C_6H_5)_3CBr\overline{|I_5 + 5Ag|} + C_2H_5OH = (C_6H_5)_3COC_2H_5 + HBr + 5AgI.$$

$$(C_6H_5)_3CI\overline{|I_5 + 5Ag|} + C_2H_5OH = (C_6H_5)_3OC_2H_5 + HI + 5AgI.$$

In order to more positively insure the identity of the carbinol ethers an attempt was made to convert them into the acetyl derivative. According to Allen and Kölliker[2] the carbinol ether reacts with acetyl chloride as follows:

$$(C_6H_5)_3C.OC_2H_5 + CH_3CO.Cl = (C_6H_5)_3COC_2H_3O + C_2H_5Cl.$$

They give figures of analysis of the substance described by them as the acetyl derivative, and also found the melting-point to be at 99° C.

The carbinol ethers obtained by me from the periodides were subjected to the action of acetyl chloride. They dissolved in acetyl chloride with an evolution of heat, but there was no ethyl chloride

[1] This Journal, 22, 768.

[2] *Ann. Chem.* (Liebig), 227, 117.

given off. On cooling, white crystals separated. These were recrystallized from petroleum ether, and the substance was obtained in snow-white, perfectly transparent prisms. The melting-point, however, was found to be not at 99° C. but at 112° C. A closer examination of the substance established the fact that it was not at all the acetyl compound, but pure triphenylchlormethane. The discrepancy between the results of Allen and Kölliker and those which I have obtained are not due to the presence of some foreign substance in the carbinol ethers which were made from the periodides. A sample of the carbinol ether was made from absolutely pure triphenylchlormethane; it was recrystallized from alcohol and from petroleum ether, was absolutely free from halogen, and melted at 83° C., as given by Allen and Kölliker. 3.2 grams of this ether gave on treatment with acetyl chloride 2.90 grams of perfectly pure triphenylchlormethane, while the calculated quantity should have been 2.95 grams.

0.2446 gram substance gave 0.7312 gram CO_2 and 0.1268 gram H_2O.

0.5600 gram substance gave 0.2870 gram AgCl.

	Calculated for $(C_6H_5)_3C.Cl$.	Found.
Carbon	81.84	81.52
Hydrogen	5.44	5.76
Chlorine	12.75	12.66

It is evident that the action of acetyl chloride proceeds as follows:

$$(C_6H_5)_3C.OC_2H_5 + CH_3COCl = (C_6H_5)_3CCl + CH_3COOC_2H_5.$$

I also tested this action on the methyl and the propyl ethers of triphenylcarbinol, and found that they, too, give pure triphenylchlormethane.

This action of acetyl chloride is entirely analogous to that of the halogen acids. Silva[1] found that hydriodic acid decomposes mixed ethers, the halogen combining with that radical which contains the smaller number of carbon atoms. Lippert[2] confirmed this also for hydrochloric and hydrobromic acids on a large number of primary and secondary ethers. But the tertiary ethers, as was shown recently by Mammontoff,[3] behave in this respect differently. They, too, are readily decomposed by halogen acids, but

[1] *Ann chim. phys.*, [5], 7, 429.
[2] *Ann. Chem.* (Liebig), 276, 148.
[3] *Journ. Russ. phys. chim. soc.*, 29, 236.

the halogen unites with the radical which contains the larger number of carbon atoms, as was shown by Mammontoff on the ethyl and propyl ethers of triphenylcarbinol,

$$(C_6H_5)_3C.OR + HX = (C_6H_5)_3C.X + R.OH.$$

The two reagents, hydrogen halide and acetyl halide, act therefore similarly upon triphenylcarbinol ethers.

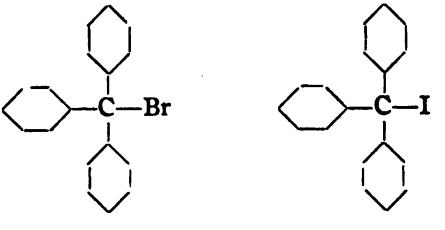
Whether the substance described by Allen and Kölliker was really the acetyl derivative or not, I cannot say. The low results which they got for hydrogen correspond better for triphenylchlormethane. An attempt will be made to prepare the acetyl derivative by some other method.

Methyl alcohol gave, with the periodides, the methyl ether of the carbinol melting at 82° C. With propyl alcohol the propyl ether was obtained.

(3). *Action of Metals.*—The action of metals upon the perhalides in neutral solvents such as ether, benzene, and acetic ester, results in the formation of the same unsaturated hydrocarbon, triphenylmethyl, which is produced when the normal halides are subjected to the same treatment. Of the different metals tried, zinc was found to give the most satisfactory results. Both periodides gave exactly the same results. The reaction is as follows:

$$(C_6H_5)_3CBrI_2 + 6zn = (C_6H_5)_3C + znBr + 5znI.$$
$$(C_6H_5)_3CI.I_2 + 6zn = (C_6H_5)_3C + 6znI.$$

From all that has been given in regard to the behavior of the two periodides we must conclude that the two react in every respect alike. Hence, they must not only have an analogous composition, but also a similar constitution. Consequently, the normal halides which gave rise to the perhalides must also have an analogous constitution:



5. TRIPHENYLIODOMETHANE.

In the first paper upon triphenylmethyl it was reported that tri-

phenyliodomethane was obtained. The yield of this product was, however, so small that only one analysis and a few qualitative tests were made. From 20 grams of triphenylchlormethane not more than 1 gram of the iodo-body was obtained. Although the reactions with ammonia and with the substituted amines, as well as the behavior of the periodide, showed conclusively that the substance produced by the addition of iodine to triphenylmethyl is the normal triphenyliodomethane, yet it appeared desirable to isolate the iodide itself in order to study its reactions directly. Of all the methods tried the following has given the best results: Triphenylmethyl is placed in a flask filled with dry carbon dioxide gas. A dilute solution of iodine in petroleum ether is added slowly to the hydrocarbon, the temperature of the flask being kept at about 60°-70° C. On cooling, there separates first a white crystalline substance, and later the iodide in clusters of large yellow prisms. The supernatant liquid is carefully decanted, the residue washed with petroleum ether, and dried in a stream of carbon dioxide. The crystals of the iodide can then be detached from the flask, and are at once put away in a closed bottle. I was able by this method to get 2.5 grams of the iodide from 2.3 grams of triphenylmethyl. The iodine was estimated by boiling the iodide with a dilute solution of sodium hydroxide containing a small amount of sulphurous acid, and precipitating the iodine in the filtered solution with silver nitrate.

I. 0.4620 gram substance gave 0.2982 gram AgI.

II. 0.5040 gram substance gave 0.3240 gram AgI.

	Calculated for $(C_6H_5)_3CI$.	Found. I.	Found. II.
Iodine	34.29	35.05	34.72

The iodide possesses a light yellow color, but on exposure to light it darkens rapidly. The color of the iodide can best be observed when the substance is placed under ether, as it is only sparingly soluble in that solvent. It is soluble in hot acetic ether, but only slightly in cold. It is quite soluble in benzene and in carbon disulphide. It melts at 132° C.[1]

With *water* it reacts exactly in the same manner as the triphenylchlor- and brommethane, and gives the carbinol. This was so pure that it melted as obtained at 161° C.

0.3443 gram substance gave 1.1003 grams CO_2 + 0.2027 gram H_2O.

[1] In my first paper the melting-point of the iodide was given as about 135° C.

	Calculated for $(C_6H_5)_3C.OH$.	Found.
Carbon	87.64	87.15
Hydrogen	6.21	6.53

With *alcohol,* on heating, it gives triphenylmethane, which, however, is due to secondary reactions, just as is the case with the periodide. But when treated with alcohol in the cold, and better still with the addition of a little molecular silver, it gives the ether of the carbinol, just like the chloride and bromide of triphenylmethane,

$$(C_6H_5)_3CI + HOC_2H_5 = (C_6H_5)_3COC_2H_5 + HI.$$

With *metals* the reaction is again perfectly similar to that of triphenylchlor- and brommethane: triphenylmethyl is formed, which, on exposure to air, gives the insoluble peroxide,

$$(C_6H_5)_3CI + Ag = (C_6H_5)_3C + AgI.$$

When in solution, the iodo-compound decomposes readily, with liberation of some free iodine. Its reaction with *oxygen* is especially interesting. When a solution of the iodide is allowed to come in contact with air, or when oxygen is passed through the solution, iodine is liberated at once, and combines with a portion of the undecomposed iodide, forming the insoluble periodide[1]; also triphenylmethyl peroxide is produced. The decomposition by oxygen is not, however, as smooth as indicated by the equation

$$12(C_6H_5)_3CI + 5O_2 = 2(C_6H_5)_3CI.I_5 + 5(C_6H_5)_3C{-}O{-}O{-}C(C_6H_5)_3,$$

but depends upon a number of circumstances, such as the nature of the solvent, whether the oxygen be dry or moist, etc. This susceptibility to the action of oxygen, no doubt, is one of the principal causes why previous attempts[2] to prepare this substance have failed.

It should be noticed that in the preparation of the iodo-compound there was also isolated a small amount of a substance which melts only a few degrees lower than the triphenylmethyl peroxide, namely at 177°-178° C., and which possesses almost exactly the same solubilities as the peroxide. There is, however, reason to

[1] The periodide comes down in exceptionally beautiful crystals, of green iridescence. Analyses point that it is more likely the tetraiodide, $(C_6H_5)_3CI.I_4$. Organic bases also give lower periodides when the iodine is not directly added, but formed slowly in the solution, as by the oxidation of hydriodic acid. So caffeine under these conditions gives the diiodide in contrast to the tetraiodide, which is ordinarily formed. This Journal, 18, 1.

[2] *Jour. Russ. Phys. and Chem. Soc.*, 29, 238.

believe that it is not the peroxide, but a decomposition product of the iodide, because it was obtained in certain reactions in which the pure iodide was employed. The small quantity available did not suffice for a complete identification of this body.

Action of Silver Chloride.—When a solution of triphenylbrommethane in benzene is shaken for several days with silver chloride, dried at 200° C., it is completely converted into triphenylchlormethane. As the bromide can be obtained very pure this method of converting it into the chloride offers one of the best methods for getting the latter absolutely pure, when it is desired for physical constants. The conversion of the iodide into the chloride is not as smooth as that of the bromide. The reaction is necessarily slow because of the practically complete insolubility of silver chloride in benzene. The longer the time of the reaction the more of the triphenyliodomethane becomes decomposed in various other ways. The chloride of silver must be as finely divided as possible. It was prepared by precipitating it in water in the usual manner, washing the precipitate successively with alcohol, absolute ether, and benzene. It was kept under benzene until needed for the reaction. 2.5 grams of triphenyliodomethane gave about 1 gram of the crude chloride. It was necessary to recrystallize the latter several times in order to free it from the accompanying decomposition products of the iodide. Individual crystals could be picked out which possessed the crystalline form, the solubilities, and the melting-point of triphenylchlormethane.

0.4410 gram substance gave 0.1867 gram AgCl.

	Calculated for $(C_6H_5)_3C.Cl$.	Found.
Chlorine	12.75	10.45

6. FORMATION OF DOUBLE SALTS.

It was already mentioned that when zinc is allowed to act upon triphenylchlormethane the zinc chloride formed in this reaction unites with a portion of the still unreduced triphenylchlormethane. This combination is a heavy oil, perfectly insoluble in benzene, only very slightly in ether, and readily in acetic ester. The compound is something in the nature of a double salt. It can also be prepared by adding a solution of zinc chloride in ether to a solution of triphenylchlormethane in any solvent. All attempts to induce the oil to crystallize have proved fruitless. This tendency

on the part of triphenylchlormethane to enter into combination with salts of metals is by no means limited to zinc chloride. A compound of this nature with aluminum chloride was described by Norris.[1] The halide salts of mercury, tin, and antimony also give such combinations. Nor is it triphenylchlormethane alone that enters with metals into these peculiar combinations. It seems to be a property apparently common to all the phenylhalogenmethanes. These compounds are quite easily formed by triphenylbrommethane, tritolylchlormethane, diphenyldichlormethane, diphenylbrommethane, and in some instances even benzotrichloride gives rise to such derivatives. There can hardly be any doubt that this forms a general reaction which is shared not only by all phenylated halogenmethanes, but will be found to belong to analogous ethane and propane derivatives. In accordance with this I find that triphenyliodomethane also gives combinations with a great many salts of metals.

Why these halogenmethanes should at all give these combinations, is a question which requires further study. We are accustomed to think that usually substances themselves basic in nature form double salts with metals. But here we have a set of bodies which are supposedly non-basic; on the contrary, they share more the properties of acyl chlorides, and yet, they behave as salts of basic radicals. It is remarkable, that all these bodies possess intense color, from yellow to dark red, irrespective of whether the metal itself is colored or not. When first formed they are oils, but on scratching or cooling, most of them change to the crystalline form. Water and alcohol decompose these salts; they can be prepared, therefore, only in such solvents as ether, benzene, carbon disulphide, etc.

Benzotrichloride gives with *antimonic chloride* an orange-red precipitate. As this is formed even in absence of benzene it cannot be due to a previous condensation of the trichloride to triphenylchlormethane.

Benzophenone Chloride, $(C_6H_5)_2C.Cl_2$, forms dark red crystalline compounds, both with antimonic chloride and with stannic chloride.

Diphenylbrommethane, $(C_6H_5)_2CHBr$, gives similar salts with

[1] *Am. Chem. J.*, 28, 54.

the above-mentioned reagents. They have not been analyzed.

The compound of *triphenylchlormethane* with *zinc chloride* could not be brought to crystallization. With *stannic chloride*, however, it is easily obtained in beautiful crystals on the addition of a benzene solution of the metal salt to one of triphenylchlormethane. The composition of this substance is identical with the one recently described by Kehrmann.[1]

0.2535 gram substance gave 0.3364 gram AgCl.

	Calculated for $(C_6H_5)_3C.Cl + SnCl_4$.	Found.
Chlorine	32.96	32.78

With *antimonic chloride*, the formation of the double salt is almost instantaneous, the precipitate consisting of fine red crystals.

0.7103 gram substance gave 0.2264 gram Sb_2S_5.

0.3261 gram substance gave 0.4785 gram AgCl.

	Calculated for $(C_6H_5)_3C.Cl + SbCl_5$.	Found.
Antimony	20.84	19.12
Chlorine	36.94	36.30

Crystalline salts were also obtained from triphenylchlormethane and *mercuric chloride*, and from *triphenylbrommethane* and *mercuric bromide*.

Tritolylchlormethane possesses, to an unusual degree, the tendency to combine with halogen salts of metals. The number of compounds which can be so obtained, is limited only by the number of salts of metals which can be brought into solution in some inert organic solvent. The salts are all intensely colored, finely crystalline, and are easily obtained exceptionally pure. The following few were analyzed.

With *zinc chloride* in acetic ester, orange-red crystals were obtained.

0.5108 gram substance gave 0.0920 gram ZnO.

0.4283 gram substance gave 0.4038 gram AgCl.

	Calculated for $(C_6H_4CH_3)_3C.Cl + ZnCl_2$.	Found.
Zinc	14.31	14.47
Chlorine	23.31	23.29

With *ferric chloride*, in dry ether, the double salt was precipitated in dark yellow, long needles.

0.3300 gram substance gave 0.7720 gram Fe_2O_3 and 0.2065 gram tritolylcarbinol.

[1] *Ber. d. chem. Ges.*, 34, 3818.

	Calculated for $(C_6H_4CH_3)_3C.Cl + FeCl_3$.	Found.
Iron	11.74	12.13
Carbinol	63.10	62.60

Mercuric chloride, in acetic ester, gives a beautiful, bright red double salt.

0.3060 gram substance gave 0.1205 gram HgS and 0.1552 gram carbinol.

	Calculated for $(C_6H_4CH_3)_3C.Cl.HgCl_2$.	Found.
Mercury	33.84	33.88
Carbinol	50.86	50.82

Triphenyliodomethane shares with the halogenmethanes this peculiar property of entering into combinations with metals. It, too, gives a series of such bodies, but in many instances the formation of the double salt is accompanied by a partial oxidation of the iodo-compound. In most instances the formation of the salts was shown only in a qualitative way, leaving, however, no room for doubt that the iodide is in this respect, as in all others, entirely analogous to triphenylbrom- and triphenylchlormethane.

Stannic chloride, even in very dilute solutions, gives a dark red crystalline precipitate.

Antimonic chloride, for the most part, decomposes the iodo-compound, with liberation of iodine.

Zinc chloride and bromide give double salts which remain as oils, but with *zinc iodide* the salt becomes crystalline on scratching the oil. It is of a dark red, almost black, color.

SUMMARY.

The experimental work detailed in this paper can now be summarized as follows:

Triphenylchlormethane and triphenylbrommethane.	The iodo-compound formed on the addition of iodine to the unsaturated hydrocarbon.
1. Empirical composition: $C_{19}H_{15}Cl, C_{19}H_{15}Br$.	1. $C_{19}H_{15}I$.
2. React with water readily and give triphenyl carbinol. With alcohol the ether is formed. With silver chloride the bromide gives triphenylchlormethane.	2. Reacts with water and with alcohol, and gives the same products as the bromide and the chloride. With silver chloride, triphenylchlormethane is formed.
3. With ammonia the amine, $(C_6H_5)_3CNH_2$, is produced.	3. Gives with ammonia the same amine, almost quantitatively.

4. React with substituted amines and give the corresponding bases $(C_6H_5)_3CNHR$.	4. Gives with amines also the same substituted bases; in some cases quantitatively.
5. The bromide gives rise to a perbromide and also to a periodide $(C_6H_5)_3CBr.Br_5$: $(C_6H_5)_3CBr.I_5$.	5. Forms with iodine, with about the same yield, a similar pentiodide, $(C_6H_5)_3CI.I_5$.
6. When acted upon by metals the chloride and the bromide give an unsaturated hydrocarbon, which, on exposure to air, forms triphenylmethyl peroxide, $(C_6H_5)_3C-O-O-C(C_6H_5)_3$.	6. Exactly the same unsaturated hydrocarbon is produced by the action of metals upon the iodo-compound.
7. Both unite with halides of metals, forming combinations of the nature of double salts.	7. Forms similar double salts.

The facts described fully justify, I believe, the following conclusions:

1. The iodo-compound is triphenyliodomethane, and its constitution must be entirely analogous to that of the corresponding bromide and chloride,

$$\begin{matrix} C_6H_5 \diagdown \\ C_6H_5-C-I. \\ C_6H_5 \diagup \end{matrix}$$

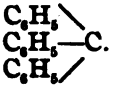
2. All the iodine added in the titration of the hydrocarbon is used up in the formation of this iodomethane; in other words, all the iodine is taken up by *one carbon atom.*

If these facts are to be interpreted in terms of the valence theory it must be admitted, that in case the hydrocarbon here described is really unsaturated, then we are dealing with a case of unsaturation which is entirely distinct in its nature from what is generally designated by this term. The unsaturation of one carbon atom in a molecule always implies a simultaneous unsaturation of another atom in the same molecule. In case of a hydrocarbon this second atom must, evidently, also be a carbon atom. We are accustomed to represent graphically such a state of unsaturation by a "double linking". In becoming saturated, as by the addition of halogens, each of the two atoms performs a similar function, each taking up one atom of halogen:

$$>C=C< + 2I = >\underset{\displaystyle I}{\overset{|}{C}} - \underset{\displaystyle I}{\overset{|}{C}}<$$

I am not aware of any exceptions to this general rule. But in the case of the unsaturated hydrocarbon under consideration *all* the

iodine, as I have shown, goes to *one* carbon atom. Hence, in the language of the valence theory, the unsaturation must be limited in this instance to one carbon atom in the molecule. The hydrocarbon must therefore, from this point of view, be represented by the constitution



The numerous facts which have been known for a long time, and which can be looked upon as supporting this view, were cited in the first paper[1] upon trivalent carbon. In a paper of recent date Thiele[2] expresses the opinion, that apart from the facts cited by me the existence of triphenylmethyl is no less supported by his theory of conjugated linkings and partial valencies. According to Thiele, we have here a case wherein the fourth valence of a methyl carbon atom is affected by the residual affinities of three phenyl carbon atoms. Such a neutralization of a valence of one carbon atom by three residual affinities of three other atoms is equivalent to a certain extent in its effect to what we have in Thiele's "conjugated system of double bonds", a stability not ordinarily present in unsaturated compounds. It will be noticed that this explanation involves a distribution of one valence of an atom in a certain indefinite way to several other atoms,—a theory not unlike Baeyer's "centric" theory of the constitution of benzene.

We may then arrange the derivatives of the hydrocarbon in a series, in order of increasing stability, something like this:

1. The unsaturated hydrocarbon, $(C_6H_5)_3C$.

2. Its ester and ether derivatives, obtained from 1. They, too, act as unsaturated.

3. Triphenyliodomethane, $(C_6H_5)_3CI$, can be obtained from 1 and 2.

4. Triphenylmethyl peroxide, $(C_6H_5)_3COOC(C_6H_5)_3$, is obtained from 1, 2, and 3.

We see that iodine can displace ethers and esters, and that oxygen can displace even iodine. The question comes up, is not the unsaturation of the hydrocarbon merely apparent unsaturation? Perhaps, we have here a case similar to Curtius' diazoacetic ester

[1] This Journal, 22, 770.

[2] *Ann. Chem.* (Liebig), 319, 134.

or to Pechmann's diazomethane. Both these substances absorb iodine[1] even in dilute solutions; in fact, they can be titrated by means of this reagent, the halogen replacing quantitatively the azo group. Perhaps the unsaturated hydrocarbon here described has the composition $(C_6H_5)_3C—R$, and this group R is being simply replaced by iodine, like the azo group in the two examples mentioned. If we assume that the R has a molecular weight equal to about one-fourth of that of triphenylmethyl, then we have an explanation why the unsaturated-like hydrocarbon takes up only four-fifths of the amount of iodine calculated for triphenylmethyl.

Against this view there are, it seems to me, a number of very valid reasons. In the first place, not taking into consideration unsaturated substances like fumaric and maleic acids, which take up no iodine at all in an alcoholic solution, there are a number of unsaturated bodies, others than triphenylmethyl, which absorb only from 10 to 80 per cent. of the calculated amount of iodine. Thus, crotonic and cinnamic acids absorb only about 8 per cent., styracine about 43, and allyl alcohol 85 per cent.[2] In the second place, by a series of experiments with different metals and with a variety of solvents, it was established that the fourth radical, if there be any, cannot come from the solvent. Thirdly, as will be shown in a paper soon to be published, this radical cannot come from the partial decomposition of triphenylchlormethane either. Strictly quantitative experiments on samples of 20 grams of triphenylchlormethane proved that the hydrocarbon can be obtained in yields of from 85 to 90 per cent. of the calculated amount.

Taking all these facts into consideration it seems to me that the constitution of the usaturated hydrocarbon is best represented as $(C_6H_5)_3C$.

Further study of the hydrocarbon itself as well as of its behavior towards different oxygen and nitrogen derivatives is in progress.

To Mr. M. Hanson, who assisted me in the prosecution of this work, I desire to express my thanks.

ANN ARBOR, MICHIGAN,
April, 1902.

[1] *J. prakt. Chem.*, 38, 422; *Ber. d. chem. Ges.*, 27, 1889.

[2] Lewkowitsch: "Chemical Analysis of Oils and Fats," p. 176.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 64.]

THE AMMONIUM TUNGSTATES.[1]

BY THOMAS M. TAYLOR.

Received March 12, 1902.

THE two general classes of ammonium tungstates are designated paratungstates and metatungstates. Laurent[2] first proposed the name paratungstates, giving to these salts the formula $5M_2O.12WO_3.nH_2O$, which was confirmed by Marignac[3] who also presented numerous other types. The metatungstates were first prepared by Margueritte,[4] but their name was suggested by Laurent. Later Scheibler and Marignac studied them and arranged them under the general formula $M_2O.4WO_3.nH_2O$. From the numerous formulas proposed for the type members, these seem best established, and the salts used in the present study conformed to them.

SOLUBILITY OF AMMONIUM PARATUNGSTATE.

$$(NH_4)_{10}W_{12}O_{41}.11H_2O.$$

The solubility of the "para salt," as given by different chemists, is as follows:

Investigator.	Ratio of salt to water.	Temperature.
Anthony	1 : 25–28	"Cold"
Lotz	1 : 26.1	10.7°
Lotz	1 : 33.3	"Cold"
Lotz	1 : 5.8–9.6	100°
Marignac	1 : 22–38	15°–18°
Taylor	1 : 59.3	26°
Taylor	1 : 69.8	21°
Taylor	1 : 74	21°
Taylor	1 : 52.7	29°
SOLUBILITY OF AMMONIUM METATUNGSTATE.		
Lotz	1 : 0.84	15°
Riche	1 : 0.35	"Ordinary"

These discrepancies are irritating. When ammonia is passed into water containing tungstic acid, a white substance remains which has been called "paratungstate," but which is remarkably insoluble. It is far more insoluble than any ammonium paratungstate met with in the present investigation.

[1] From the author's thesis presented for the Ph.D. degree, 1901.

[2] *Ann. chim. phys.* [3], **21**, 54 (1847).

[3] *Ibid.* [3], **69**, 24 (1863).

[4] *Ibid.* [3], **17**, 475 (1846).

AMMONIUM PARATUNGSTATE.

$(NH_4)_{10}W_{12}O_{41}.11H_2O$.

When a solution of "para salt" is evaporated at slightly elevated temperature, monoclinic needles crystallize out; when evaporated at a boiling temperature, flat plates appear. These needles have been described as orthorhombic prisms by Kerndt, Schabus and Marignac. Examined microscopically in polarized light they show an apparent parallel extinction, and give a biaxial interference figure, with the acute bisectrix parallel to the long axis of the crystal, and therefore appear to be orthorhombic, but give these orthorhombic reactions on account of their remarkable twinning structure, which closely resembles the wedge-shaped penetration figures seen in the hydrated zeolites,—more particularly stilbite, which is orthorhombic in form but is a complicated monoclinic twin. It is an interesting fact that these ammoniated and hydrated crystals exhibit the same internal structure as the hydrated zeolites.

Crops of crystals usually consist of mixtures of needles and plates in varying proportion; many previous analyses have undoubtedly been made with such material. Such a mixture, consisting largely of needles, was digested for three days in forty times its weight of water. The water was removed and the same amount added and allowed to stand again for three days. The needles remaining contained no admixed plates. This separation does not prove that the plates are the more soluble, for they are smaller and would therefore dissolve out first. But whatever the reason for this separation, the purpose in view was accomplished: the needles were isolated. These on analysis gave the following data:

Tungsten trioxide, determined by ignition in a porcelain crucible:

"Para needles." Grams.	WO_3. Grams.	WO_3. Per cent.
4.0016	3.4395	85.95
3.1344	2.6938	85.94

The ammonia was determined by the usual distillation and titration method.

"Para needles." Grams.	NH_3. Gram.	NH_3. Per cent.
2.9265	0.15370	5.25
2.1002	0.10983	5.23

The water was determined as follows: The salt was covered with lead oxide, and ignited in a combustion tube in a current of dry air; the water and ammonia were caught in sulphuric acid and weighed. Subtracting from this weight that of the ammonia, the weight of the water was obtained.

"Para needles." Grams.	$NH_3 + H_2O$. Gram.	Water. Per cent.
1.2458	0.1813	9.31
1.0636	0.1536	9.20
1.5988	0.2262	8.91

These values correspond to the formula $(NH_4)_{10}W_{12}O_{41}.11H_2O$, which requires WO_3, 85.87 per cent.; NH_3, 5.24 per cent.; H_2O, 8.88 per cent.; and are also a confirmation of Marignac's formula.

When the "para needles" are crystallized from boiling water, monoclinic plates separate (extinction parallel to diagonal of rhombic section, axial plane lying in the plane of symmetry), and to obtain these with no admixed needles, it is necessary to keep the water at the boiling-point, and to remove the plates from the boiling solution as fast as they are formed. Some plates prepared in this way, gave on ignition the following per cent. of tungsten trioxide:

"Para plates." Gram.	WO_3. Gram.	WO_3. Per cent.
0.6931	0.6170	89.02
0.2528	0.2249	88.96
0.3216	0.2816	88.93
0.5905	0.5253	88.96

The theoretical requirement of tungsten trioxide for $(NH_4)_{10}W_{12}O_{41}.5H_2O$, is 88.83 per cent. and this also confirms Marignac's formula. On comparison, these two para salts show as follows:

"Para needles." $(NH_4)_{10}W_{12}O_{41}.11H_2O$.

"Para plates." $(NH_4)_{10}W_{12}O_{41}.5H_2O$.

Thus it would appear that the "para needles" in boiling water, lose 6 molecules of water.

AMMONIUM METATUNGSTATE.

$(NH_4)_2W_4O_{13}.8H_2O$.

Margueritte[1] first prepared this salt by boiling the para salts with tungstic acid. Laurent[2] prepared it, by the continued boiling of the aqueous solution of the para salts. Scheibler[3] made it by heating the para salt to 250°, until ammonia was given off, causing

[1] *Ann. chim. phys.* [3], 17, 475 (1846).
[2] *Ibid.* [3], 21, 62 (1847).
[3] *J. prakt. Chem.*, 83, 304 (1861).

a partial separation of tungstic acid, then dissolving the residue in water and allowing it to crystallize. This method was adopted by Persoz[1] and later by Marignac[2].

Scheibler describes the salt as crystallizing in large tetragonal octahedra, which effloresce in the air. If the crystals have been scratched or bruised, they quickly lose water and become opaque. Marignac observed that the crystals lose 7 molecules of water at 100°, and the remaining molecule is not driven out below 200°. Riche noticed the same behavior. When alcohol is added to a hot solution of the "meta salt", the salt $(NH_4)_2W_4O_{13}.6H_2O$ separates, and, according to Marignac, loses 5 molecules of water at 100°.

In the present investigation the "meta salt" was prepared by boiling an aqueous solution of the "para salt" for two or three days, evaporating to small bulk and allowing the syrupy liquid thus obtained to stand. Large transparent tetragonal octahedra were obtained. After three or four recrystallizations, the crystals became almost colorless, but the yellow tint was difficult to remove. Boiled with purified bone-black the greater part of the original brown color may be removed. The crystals have a high index of refraction, which is true also of their solution. These crystals of "meta salt" were also prepared by heating the "para needles" at 150°, for four hours.

On analysis the salt gave 3.05 per cent. of ammonia.

"Meta salt." Gram.	NH_3. Gram.	NH_3. Per cent.
0.5016	0.01531	3.05

This corresponds to $(NH_4)_2W_4O_{13}.8H_2O$, which contains 3.02 per cent. of ammonia, confirming Scheibler's formula. The characteristic physical properties were in such accord with the published data that further analysis was not undertaken.

COLLOIDAL AMMONIUM TUNGSTATE.

$(NH_4)_2W_6O_{19}.4$ or $6H_2O$.

On repeating the method of Scheibler to obtain the "meta salt" (*i. e.*, heating the "para needles" to 250°), a colloidal "gum" was obtained. As many as twenty experiments failed to substantiate his claims, for the "meta salt" was produced at 150°. This "gum" would dry hard, become transparent and had a high index of re-

[1] *Ann. chim. phys.* [4], 1, 101 (1864).
[2] *Ibid.* [4], 3, 72 (1864).

fraction. It did not cement itself to porcelain, in the way "colloidal tungstic acid" is said to do, but would shrink away from the sides of the containing vessel, and could easily be removed. Under the microscope "para needles" were found embedded in it, and were removed by dialysis. The fraction passing through the parchment paper in a few hours, crystallized in tetragonal octahedra; later fractions in "para needles," and still later fractions would not crystallize at all but consisted largely of "gum" which had passed through. This "gum" therefore, when first prepared, consists of a mixture of "para salt," "meta salt," and a "colloidal salt."

The best condition for getting a large yield of the "gum" is as follows: Pulverized "para needles" are spread out on a watch-glass, and heated in an air-bath at 220° for one hour. The air-bath must allow the escape of water and ammonia. The product is covered with water and boiled vigorously for fifteen or twenty minutes, when a clear, but dark, heavy liquid results. This is filtered away from any residue and on evaporation dries into the "gum" with an almost quantitative yield. On standing several days in water, the residue will pass into the "gum" without previous boiling. At higher temperatures considerable tungstic acid is separated and the yield is not so good. The "meta" salt free from "para" must be heated to 250°, before yielding the "gum," and the yields are nothing like so large, as when the "para salts" are taken for the starting-out material.

A marked darkening of the original white salt is noticed after heating. Different fractions of the "para salts" yield the "gum" with different degrees of readiness. These facts point to the presence of some impurity which may affect the transformations.

After dialyzing a portion of the "gum" for six days it gave the following analysis:

"Gum." Gram.	WO_3. Gram.	WO_3. Per cent.
0.6150	0.5447	88.57
"Gum." Grams.	**NH_3. Gram.**	**NH_3. Per cent.**
0.4825	0.01279	2.65
1.3776	0.03848	2.79

Another sample was dialyzed for thirteen days, through parchment paper, using ten changes of water of 2½ liters each. The dialyzer had a diameter of 15 cm. After four or five days, the increase of volume in the inner vessel ceased. The resulting col-

loidal salt, when dried on the water-bath and allowed to stand in the air, slowly increased in weight. When dried at the ordinary temperature and allowed to stand, it decreased in weight. A portion of the "colloidal salt," dried on the water-bath, gave the following analysis:

"Colloidal salt." Gram.	WO_3. Gram.	WO_3. Per cent.
0.4469	0.4089	91.49
0.4523	0.4143	91.60
"Colloidal salt." **Gram.**	**NH_3.** **Gram.**	**NH_3.** **Per cent.**
0.6334	0.01520	2.40
0.5985	0.01415	2.36

These results point to the formula $(NH_4)_2W_6O_{19}.4H_2O$, which requires ammonia 2.24 per cent. and tungsten trioxide 91.82 per cent.

In the same way another portion of "gum" was dialyzed for fourteen days, using nearly double the amount of water previously used (twelve changes of water of 3½ liters each). The resulting "colloidal salt" dried at the ordinary temperature gave the following analysis:

"Colloidal salt." Gram.	WO_3. Gram.	WO_3. Per cent.
0.1227	0.1101	89.73
0.2100	0.1885	89.76
"Colloidal salt." **Grams.**	**NH_3.** **Gram.**	**NH_3.** **Per cent.**
0.9243	0.01996	2.16
1.0301	0.02184	2.12

These percentages are close to the formula $(NH_4)_2W_6O_{19}.6H_2O$, which requires ammonia 2.29 per cent., and tungsten trioxide 89.69 per cent. This sample was dried at the ordinary temperature, the previous one at 100°. Since the salt loses weight on standing, it is likely that the additional water does not represent such a definite number of molecules as these analyses would indicate.

To compare the percentage of ammonia, in the different salts, the following table is given:

Salt.	NH_3. Per cent.
"Para needles"	5.24
"Para plates"	5.42
"Meta salt"	3.02
"Colloidal salt" (dialyzed six days)	2.72
" " (" thirteen days)	2.38
" " (" fourteen days)	2.14

The dialyzed salt dries hard and clear like glass, with a yellowish tint, contains no embedded crystals, and under no conditions could it be made to crystallize. It has a high index of refraction and is miscible with water in nearly all proportions. It may prove of value as a mounting medium in microscopic work, and also for the mechanical separation of minerals.

Its solution has an acid reaction and absorbs ammonia with avidity. One long series of dialyzations was spoiled, by working with ammonia in the same room, the "colloidal salt" changing to the "meta" and "para" salts. By treating the solution of the "colloidal salt" with tenth-normal ammonia, till the acidity is barely neutralized, it passes into the "meta salt". Unless care is used considerable amounts of the "para salts" will be formed.

Under certain conditions the "colloidal salt" passed into a white modification, which on microscopical examination proved to be an emulsion, the globules closely resembling fat globules. On drying, the white emulsion gradually passed into the transparent variety. The emulsion can be produced by cooling a clear concentrated solution with ice-water. Frequently a more dilute solution, would be filled with spurious clouds, floating in suspension, which appeared to be some foreign matter. This could not be filtered out and was a source of annoyance, until it was examined microscopically, and found to be the emulsion. Emulsions are common enough among organic substances, but are rarely observed with inorganic salts.

At first it was thought that this "colloidal salt" might be "colloidal tungstic acid," but since after prolonged dialysis, the ammonia could not be removed, it was taken to be a colloidal ammonium tungstate.

The history of "colloidal tungstic acid" is of some interest. Graham,[1] in 1864, reported the existence of "colloidal tungstic acid," which he prepared by treating a 5 per cent. sodium paratungstate solution with dilute hydrochloric acid and dialyzing the mixture. The resulting heavy liquid had such a high specific gravity, that glass would float on it. Sabanejeff[2] made a molecular weight determination using cryoscopic methods, and reported the formula $3WO_3.H_2O$. Later[3] he retracted his determinations,

[1] *Proc. Roy. Soc.*, London, 13, 340 (1864).
[2] *J. Russ. Chem. Soc.*, 21, 1 (1889).
[3] *Ztschr. anorg. Chem.*, 14, 354 (1897).

and published an article on the "Non-Existence of Colloidal Tungstic Acid," saying that he had previously taken Graham's word for the composition of the "gum." On examination he found it was impossible to dialyze out the sodium, and concluded that it was amorphous sodium metatungstate. His proof of this is open to criticism, for: he states that the salt had a marked acid reaction; his analyses do not conform closely to the theoretical for sodium metatungstate; and the periods of dialysis used were not long enough to thoroughly separate the material. The conversion of one form into the other was rather violent. Sabanejeff changed the amorphous salt into the crystallized variety, by heating to 130°-150°, in a sealed tube with an excess of water. This temperature is about the same as that which changes the ammonium "para salt" to the "meta salt" and seems altogether too high to prove the dimorphism, of the two sodium salts. Had the acidity of his colloidal salt been gradually neutralized with sodium bicarbonate or carbonate, the salt might have reverted to the crystallized form, and its dimorphism thus been disproved. It seems probable that his dimorphous colloidal sodium metatungstate may prove to be a colloidal sodium tungstate analogous to the colloidal ammonium tungstate prepared in the present investigation.

TEMPERATURE AT WHICH THE AMMONIUM SALTS BEGIN TO LOSE AMMONIA.

Some "para needles" were placed in a glass U-tube immersed in an oil-bath and dry air was rapidly passed over them into Nessler's solution. It was found that if the glass tube leading into the solution, was etched on the inner surface, a brown ring would form on the roughened surface, several minutes before the solution showed any traces of color. The moment of formation of this brown ring, was taken as the signal for the first appearance of ammonia, and the temperature of the bath noted. In this manner the "para needles" began to lose ammonia at 60°. The "para plates" at the same temperature, and the "meta salt" at 120°.

It is significant that the "meta salt" should begin to lose ammonia at 120° as it was prepared at 150°. It seems improbable that a salt which begins to lose ammonia at 120° could be made at 250°, as recorded by Scheibler.

Marignac and others dry the "para salts" at 100° and attribute the loss to expulsion of water, but a part of that loss is ammonia.

However, the ammonia that escapes below 100° is but a trace.

ACTION OF DRY AMMONIA GAS ON "PARA NEEDLES."

The effect of ammonia on "para needles" was determined as follows: A boat, filled with needles, was placed in a bent tube immersed in paraffin. Ammonia gas (dried by lime and caustic potash) was passed over it, and escaped through 0.75 cm. mercury and 9.00 cm. of water, so that the gas was under a pressure of about 14 mm. of mercury, in excess of the atmospheric pressure. After heating for one and a half hours the boat was placed in a capsule and weighed. The percentage of ammonia was then determined. The loss in weight, together with the percentage of ammonia furnish data, from which the changes in the salt may be calculated.

ACTION OF DRY AMMONIA GAS ON AMMONIUM PARATUNGSTATE.

Temperature.	"Para needles." Grams.	Weight after treatment.	NH_3. Gram.	Molecules of NH_3 added.	Molecules of water lost.	Approximate formula.
			Original "para needles."			$10NH_3.12WO_3.16H_2O$
100°	0.7193	0.6904	0.01276	+1.3	— 8.5	$11NH_3.12WO_3.7H_2O$
110°	1.0012	0.9632	0.06295	+2.0	— 8.7	$12NH_3.12WO_3.7H_2O$
120°	1.1203	1.0796	0.07268	+2.4	— 8.8	$12NH_3.12WO_3.7H_2O$
130°	0.9936	0.9619	0.06901	+3.2	— 8.8	$13NH_3.12WO_3.7H_2O$
140°	0.8391	0.8101	0.05563	+2.7	— 8.7	$13NH_3.12WO_3.7H_2O$
150°	1.2278	1.1768	0.07514	+1.7	— 9.1	$12NH_3.12WO_3.7H_2O$
160°	1.2204	1.1696	0.06530	+0.2	— 7.7	$10NH_3.12WO_3.8H_2O$
200°	0.9730	0.9251	0.01797	—0.6	— 8.3	$9NH_3.12WO_3.8H_2O$
250°	1.3238	1.2286	0.05872	—1.6	—11.5	$8NH_3.12WO_3.4H_2O$

Attention is directed to the nearly constant loss of water; and that at 130° the maximum amount of ammonia is absorbed. Tungsten trioxide was separated at 250°.

These ammonia-addition salts are quite unstable; when dissolved in water, the water is made alkaline and "para needles" crystallize out; when allowed to stand in the air they revert to their original weight, and percentage of ammonia, as evidenced in the following experiments: Two boats containing "para needles" placed side by side in the same U-tube were heated together in dry ammonia gas at 130° for one and a half hours. The ammonia in one was determined at once; the companion boat was allowed to stand over night, before determining the ammonia.

	"Para needles." Gram.	NH_3. Gram.	NH_3. Per cent.
Boat A.	0.8754	0.06242	7.13
Companion Boat A.	0.9718	0.05034	5.18
Boat B.	0.8744	0.05859	6.70
Companion Boat B.	0.9321	0.04866	5.22

Companion Boat B, after standing over night, weighed 0.9319 gram. It appears therefore that the salt has lost its added ammonia, and absorbed its lost water.

ACTION OF MOIST AMMONIA GAS ON THE "META SALT" AT THE ORDINARY TEMPERATURE.

A boat containing 0.9874 gram of "meta salt" was placed in a vacuum desiccator, over ammonium hydroxide. After standing several hours, the transparent crystals were found to be replaced by a white salt covered with water. This water was removed by spontaneous evaporation in the air, and the residue weighed 0.9327 gram and contained 0.04803 gram ammonia, equivalent to 5.15 per cent., or 3.83 molecules of ammonia added. Hence the "meta salt" has been changed by moist ammonia gas, at the ordinary temperature into the "para needles," and the conversion has been practically quantitative.

The "para needles" being a hundred times more insoluble than the "meta salt," have crystallized out from the water of crystallization of the latter. In other words the water of the old salt has been pushed out by the new salt, and the new salt is found "swimming" in the water of crystallization of the old salt. After standing several days the amount of water in the boat gradually increased, so that water evidently slowly distils into the boat.

ACTION OF MOIST AMMONIA GAS ON THE "META SALT" AT 100°.

"Meta salt" treated with ammonia passes to the "para needles;" the latter in solution change at 100° to the "para plates" so that the action of moist ammonia on the "meta salt" at 100° can almost be predicted. A boat containing 0.4408 gram of "meta salt" (placed in the same apparatus used for determining the action of dry ammonia on the "para needles") was treated with moist ammonia gas at 100°, for one hour. After treatment, the salt weighed 0.4189 gram; after standing sixty hours in the air it weighed 0.4186 gram. This contained 0.02276 gram of ammonia equivalent to 5.44 per cent., or 4.04 molecules of added ammonia.

Hence at 100° moist ammonia gas transforms the "meta salt" into the "para plates." Dry ammonia gas would probably form the ammonia-addition product produced at that temperature.

THEORETICAL CONSIDERATIONS.

NORMAL AMMONIUM TUNGSTATE.

The normal sulpho-salt $(NH)_2WS_4$ exists and one might expect the existence of the corresponding oxygen salt. However, normal ammonium tungstate has never been prepared. Marignac,[1] by the spontaneous evaporation of a solution of "para salt," in a bell-jar over lime (which would absorb water and not ammonia), obtained a salt of the composition $2(NH_4)_2O.3WO_3.3H_2O$. This salt was soluble in cold water but soon changed to the "para salt." In the air it gave off ammonia reverting to the "para salt."

The ratio between the ammonia and tungsten trioxide, in the different salts is tabulated as follows:

Salt.	NH_3.	:	WO_3.
Theoretical normal salt	1.0	:	0.5
Marignac salt (unstable)	1.0	:	0.75
"Meta salt"	1.0	:	2.0
"Para salt"	1.0	:	1.2

It is seen from these ratios that Marignac's salt approaches more closely to the normal ratio than any salt which has yet been prepared, but it was not stable at the ordinary temperature. Of the other salts, the "para-salt" follows next in order.

The para ammonio-addition salts prepared in this investigation are unstable, easily losing their excess of ammonia. It seems therefore that at the ordinary temperature, tungsten can not hold any more ammonia than that expressed by the para ratio. It is believed that the formation and preservation of the normal salt is simply a question of temperature.

WATER OF CRYSTALLIZATION.

In boiling water the "para needles" lose exactly 6 molecules of water and crystallize out as "para plates." Five molecules of water remain in the salt, and it is significant that 5 ammonium oxide molecules remain also. Possibly 5 ammonium oxide molecules influence 5 water molecules in such a manner, that the latter are more firmly bound or linked than the others. Whatever ex-

[1] *Ann. chim. phys.* [3], **69**, 22 (1863).

planation may be advanced, the fact remains that 6 molecules of water are driven out at 100°, and 5 are not.

The "meta salt" $(NH_4)_2W_4O_{13}.8H_2O$ at 100° loses 7 molecules of water. The remaining molecule can not be driven out below 200°. The "meta salt" from alcohol, $(NH_4)_2W_4O_{13}.6H_2O$, loses at 100° 5 molecules of water, and the remaining molecule behaves as before. In these salts 1 molecule of water must be very differently combined from the others, for one requires 200° of temperature to remove it, while the others leave the salt quite rapidly even at the ordinary temperature. The number of water molecules remaining again correspond to the number of ammonium oxide molecules, and the probability increases that 1 ammonium oxide molecule influences 1 hydrogen oxide molecule.

These two salts may be written:

$$[2NH_4OH.4WO_3].[7H_2O]$$
$$[2NH_4OH.4WO_3].[5H_2O]$$

At 100° in the air the water is split off from both salts, and the common residue or nucleus $[2NH_4OH.4WO_3]$ remains, which is stable at 200°.

AMMONIA CONTENT.

The "para needles" and "plates" begin to lose ammonia at 60°; the "meta salt" at 120°. If the ammonia in these salts is combined in the same manner, it ought to be given off at the same temperature. Such is not the case, and consequently it looks as though part of the ammonia was combined or linked differently from the rest. At 150° the "para salts" lose 4 molecules of ammonia, and revert to the "meta salt." The "meta salt" on the addition of 4 molecules of ammonia advances to the "para salt." The commonest double salt of sodium with ammonium paratungstate, has the composition $Na_4(NH_4)_6W_{12}O_{41}.15H_2O$ (Knorre, Marignac, Hallopeau). Four molecules of ammonia have been replaced by 4 molecules of sodium. The fact that all the ammonia has not been displaced by sodium, indicates that 4 molecules are differently combined than the others, and probably these are the same 4 which are lost at 150° (or on long standing in water, even at the ordinary temperature).

TRANSFORMATIONS.

The transformations in this series of salts are of interest. The

entire series may be prepared from the first member or the entire series may be prepared from the last member. In fact, the whole series may be prepared from any member.

Temperature of formation.	Series.		
(Below 100°)	"Para needles"	$(NH_4)_{10}W_{12}O_{41}$.	$11H_2O$
(100°)	"Para plates"	$(NH_4)_{10}W_{12}O_{41}$.	$5H_2O$
(150°)	"Meta salt"	$(NH_4)_2W_4O_{13}$.	$8H_2O$
(220°)	"Colloidal salt"	$(NH_4)_2W_8O_{25}$.	4 or $6H_2O$

Before taking up the transformations, attention may be called to the difference between the last two salts. This difference is $2WO_3.2$ or $4H_2O$. Gibbs[1], in his classic work on the complex inorganic acids, pointed out the existence of a "homologous series" of metatungstates having a common difference $2WO_3.RO$. The difference noticed here, while not exactly the common difference discovered by him, is equivalent to it, as far as the tungsten trioxide is concerned.

The two "para salts" (in the series) on long standing in solution, at the ordinary temperature revert to the "meta salt." The "colloidal salt," on absorbing ammonia, reverts to the "meta salt." The "meta salt" on standing reverts to the residue $[2NH_4OH.4WO_3]$. This residue, therefore, may be considered a decomposition product or nucleus of the whole series. It is the most stable portion in the entire series; when it is attacked, the structure of the salt is broken down, and tungstic acid separates. It is well known that the "meta salts" are broken down by acids or alkalies only with difficulty.

Beginning with the first member, we may go down the series by physical means: "Para needles" heated to 100° (in water) go into the "para plates." The "plates" at 150° (in air) pass into the "meta salt." The latter heated to 250° changes to the "colloidal salt."

Again we may proceed down the series by chemical means. "Para needles" treated with acetic acid go to the "para plates."[2] The "para plates" boiled with tungstic acid or dilute mineral acids pass into the "meta salt." The "meta salt" as yet has not been changed into the "colloidal salt" by chemical means; boiling with tungstic acid did not produce it.

[1] *Proc. A. A. A. S.*, 47, 1 (1898), and previous papers.

[2] Gibbs: *Am. Chem. J.*, 1, 229 (1879). Gibbs states that the salt formed with acetic acid has the composition $(NH_4)_{10}W_{12}O_{41}.6H_2O$, and adds that it appears to be the same salt, to which Marignac attributed $5H_2O$. The temperature of crystallisation may clear up the discrepancy.

To reverse the transformations: Beginning with the last member we may proceed up the series by chemical means. The acidity of the "colloidal salt" neutralized with ammonia, produces the "meta salt." The "meta salt" on the addition of 4 molecules of ammonia at 100° advances to the "para plates." The "para plates" on the addition of water at the ordinary temperature proceed to the "para needles."

From these considerations it appears probable that a common nucleus runs through the whole series, and that the nucleus is $[2NH_4OH.4WO_3]$. The molecular weight of this nucleus is as yet unknown; it may be a polymer, or it may be one-half, which would correspond to Gibbs' difference $[RO.2WO_3]$, and might be written

$$\begin{matrix} NH_4 \\ H \end{matrix} > O.2WO_3.$$

The simplest view of the matter would favor the nucleus $[NH_4OH.2WO_3]$, and until molecular weight determinations have been made, the salts may be written with this in mind.

AMMONIUM "PARA" AND "META" TUNGSTATES.

Temperature of formation.		
(Below 100°)	"Para needles"	$6[NH_4OH.2WO_3].4[NH_4OH].6[H_2O]$
(100°)	"Para plates"	$6[NH_4OH.2WO_3].4[NH_4OH]$
(150°)	"Meta salt"	$2[NH_4OH.2WO_3].7[H_2O]$
(220°)	"Colloidal salt"	$2[NH_4OH.2WO_3].2[WO_3].3$ or $5[H_2O]$

PARA-AMMONIO-ADDITION-PRODUCTS.

In ammonia gas.	
(100°)	$6[NH_4OH.2WO_3].[NH_4OH].4[NH_3]$
(110°)	$6[NH_4OH.2WO_3].[NH_4OH].5[NH_3]$
(120°)	$6[NH_4OH.2WO_3].[NH_4OH].5[NH_3]$
(130°)	$6[NH_4OH.2WO_3].[NH_4OH].6[NH_3]$
(140°)	$6[NH_4OH.2WO_3].[NH_4OH].6[NH_3]$
(150°)	$6[NH_4OH.2WO_3].[NH_4OH].5[NH_3]$
(160°)	$6[NH_4OH.2WO_3].2[NH_4OH].2[NH_3]$
(200°)	$6[NH_4OH.2WO_3].2[NH_4OH].[NH_3]$
(250°)	$4[NH_4OH.2WO_3].4[WO_3].4[NH_3]$

PARA-AMMONIO-SUBSTITUTION SALT.

(Below 100°)	$6[NH_4OH.2WO_3].4[NaOH].10[H_2O]$

These tables suggest the presence of "nuclei" and "side-chains." The "para salts" appear to be polymers of the "meta salts," linked together by, or to which are added, the "side-chains." The "side-chains" may be split off by physical or chemical means, and

substitutions appear to take place in them. Where transformations require the splitting off of part of the structure, both physical and chemical means may be employed to accomplish the desired end. But where transformations demand the addition of these parts, then chemical means only can accomplish the purpose.

Smith[1] and Hardin have demonstrated the tendency of tungsten trioxide itself to polymerize. And after such polymerization the material is insoluble in sulphur monochloride, whereas before, it is soluble. The polymerized ammonium salts in this series are over a hundred times more insoluble than the unpolymerized.

It is significant that the temperature which breaks down the "para salt" into the "meta salt" (*i. e.*, 150°) is not far from that temperature (130°) at which the "para salt" in ammonia gas is able to take on the maximum amount of ammonia. In other words, the polymer absorbs the most ammonia at a temperature near its rupture temperature. It looks as though the polymer when "opened up" was enabled to add more ammonia.

There is no reason why the compounds of carbon should have a monopoly over "homologous series," "polymerizations," "ring formations," "side-chains," "substitution products" or "gums."

Organic "gums" are supposed to be high polymers of some simple form, and the polymerization is usually accompanied with insolubility and non-crystalline character. The "gum" in the present investigation appears to be an ammonium salt, but no surprise will be expressed if it proves to be an acid salt of "colloidal tungstic acid" and ammonium metatungstate. If "colloidal tungstic acid" exists, it would probably be a polymer of tungsten trioxide and its affinity for ammonia would be so great that only with difficulty could the two be separated. In one experiment, a long process of dialyzation was ruined by the presence of ammonia in the atmosphere of the room, and who knows how much ammonia the other experiments absorbed? Traces of ammonia would neutralize the work performed by days of dialyzation. The subject needs to be further investigated.

It is hoped that benzylamine tungstate will form a similar series of salts, and, yielding more readily to organic methods, facts concerning their molecular magnitude and constitution may be developed.

UNIVERSITY OF PENNSYLVANIA.

[1] This Journal, 21, 1007 (1899).

THE APPLICATION OF ESCHKA'S METHOD TO PIG IRONS.

By [illegible]

Received April 21, 1900.

Of the three methods generally used for the determination of sulphur in pig iron,—the evolution method, the oxidation method in the wet way, and Bamber's method,—it is generally known that at least two of them are not always accurate.

The evolution method does not, for some irons, give accurate results. The amount of sulphur evolved as hydrogen sulphide plus that remaining unacted on in the residue is less than the amount obtained by either the oxidation or Bamber's method. This error is especially noticeable in those irons containing a high percentage of combined carbon.

The oxidation in the wet way does not, with some irons, effect the complete oxidation of the sulphur, a portion of it remaining with the residue of graphite and silica. Bamber's method is generally used when the oxidation method does not effect its purpose, and no doubt is the safest, besides doing away with the precipitation of the sulphur by barium chloride from a concentrated solution of ferric chloride. When a platinum dish is available, it affords a simple method.

The thought occurred to the writer that if it were possible to reduce the sample of pig iron to a fine powder, its oxidation might be effected in the presence of a basic mixture, such a mixture for example as magnesia and sodium or potassium carbonates. The sulphur, it was hoped, would be converted into soluble sulphates of the bases present, and any small quantity of sulphides of these metals formed could be oxidized by bromine, as in the determination of sulphur in coke. The writer has been informed that v. Reis[1] has already applied this modified Eschka method to pig irons, but his paper is not accessible to me.

Two mixtures were made as follows: One of magnesia 2 parts and sodium carbonate 1 part, well ground and mixed, and another of magnesia 4 parts, potassium carbonate 1 part and sodium carbonate 1 part. The addition of potassium carbonate, it was thought, would hasten the oxidation, potassium carbonate having a slight solvent action on ferric oxide. It was first thought that the samples of pig irons had to be ground very fine, and to accom-

[1] Stahl und Eisen, 8, 897.

plish this the agate mortar was used, with the result that with a great deal of labor a small sample was finally obtained. Upon treating this sample of about 1 gram with the mixture of magnesium oxide and sodium carbonate, in a platinum crucible at a full red heat, it was found that oxidation was rapid, about fifteen minutes being required to effect it. After a little experimenting it was found that samples of 80 and 60 mesh were oxidized completely, while samples of 30 mesh were not. In fact 50 mesh seemed to be the limit of coarseness of sample.

The samples of basic pig irons as delivered to this laboratory have been crushed in a steel mortar, a pestle and hammer being used. The operation requires about five minutes for a 20-gram sample of 60 mesh. This is done because we wish to have a sample that has been treated under as nearly as possible the same conditions as our basic pig irons. A sample so treated, quite frequently cannot be drilled.

For carrying out the experiments herein described, four samples of gray irons were thus prepared of 80 and 60 mesh each. A given quantity of each iron was all ground to pass through an 80-mesh seive and a 60-mesh sample was prepared in the same way.

No. 1. Gray forge pig iron: Si, 1.22; S (?).

No. 2. Chilled basic pig iron: Si, 0.55; S (?).

No. 3. Sample C of the American Foundrymen's Association: Si, 1.783; S, 0.076.

No. 4. Sample B of same: Si, 1.076; S, 0.056.

The following method was finally decided upon: 3 grams of the sample of a fineness higher than 50 mesh are weighed into a platinum crucible of 30 cc. capacity and 3 grams of the basic mixture are added. The greater part of this mixture is added at once and the whole thoroughly mixed. The balance, about 0.5 gram, is used in covering the top of the mixture. The crucible is then placed over a Bunsen flame, a shield being used to prevent the products of combustion of the flame from coming in contact with the mixture. A description of this shield will be given later. The part of crucible exposed to the flame is heated for one hour at a full red heat. At the end of this time the mass will be found sintered together, and can be broken up when cold with a glass rod, extracted with hot water into a No. 2 beaker, and 10 cc. of bromine water added. It is best to always add a fixed amount as bromine frequently contains sulphur, and by using the

same amount in a blank determination this error will be eliminated. The solution is boiled for fifteen minutes on the hot plate and filtered, taking care to see that the filtrate is perfectly clear. The residue is washed with hot water, and to the filtrate 1.5 cc. of concentrated hydrochloric acid are added. The bromine is expelled by boiling, and sulphur is precipitated in the boiling solution by 10 cc. of a hot 10 per cent. solution of barium chloride.

The products of combustion of the gas must be kept away from the contents of the crucible. This can be done without the use of a shield if care is used, at least when gasoline is used for furnishing gas.

It was decided to treat samples Nos. 1 and 2 by each of the following methods:

First. Evolution Method.—Absorption of hydrogen sulphide in solution of potassium hydroxide, oxidation of the potassium sulphide formed by potassium permanganate solution, acidifying with hydrochloric acid, clearing with oxalic acid, neutralizing with ammonia, making slightly acid with hydrochloric acid and precipitation of the sulphur as usual. The sulphur in the residue is determined and added to that obtained as hydrogen sulphide, 10 grams of the sample being used.

Second. Oxidation in the wet way by solution in concentrated nitric acid with the addition of 3 grams of potassium chlorate when solution is complete, and the usual evaporation and resolution with the final precipitation of the sulphur in the 100 cc. solution, using a hot saturated solution of barium chloride and having the ferric chloride solution just short of boiling. The sulphur is determined after standing twelve hours.

Third. Bamber's method as described by Blair, third edition.

SAMPLE NO. 1.

Evolution method + S in residue.	HNO_3 and $KClO_3$.	Bamber's method.	Oxidation in presence of basic mixture.	Time used in ignition.	Fineness of sample.	Mixture used.		Shield.
0.035	0.036	0.035	0.039	1.5 hr.	80 mesh.	MgO & Na_2CO_3.		No
0.036	0.035	0.036	0.039	1.5 hr.	"	"	"	No
0.036	0.035	0.034	0.040	1 hr.	"	"	"	No
0.035		0.035	0.042	1 hr.	"	"	"	No
....		0.036						
Average:								
0.035	0.035	0.035	0.040					

It was thought that the increase of sulphur as shown by this method was due to the flame, the basic mixture absorbing sulphur therefrom. To prevent this an asbestos board 8 inches by 4 inches was used; in the center of this board and near the lower edge a clean hole was cut, of a size sufficient to admit the crucible for about seven-eighths of its length, and forming a snug fit. To the upper edge of this board was hinged, by means of a copper wire, a board of the same length but 3 inches wide and without any hole. The whole arrangement represents an "A" tent affair, open at both ends, which can be placed over the tripod in such a manner that when the crucible is put into place about seven-eighths of its length projects through the board and rests upon the platinum triangle. The products of combustion from gas pass off above and away from the crucible.

The results obtained on sample No. 1, using the shield, were as follows:

SAMPLE NO. 1.

Nos.	Oxidation in presence of basic mixture.	Fineness of sample.	Time of ignition.	Mixture used.
1.....	0.0399	60 mesh	1½ hours	MgO, K_2CO_3 & Na_2CO_3
2.....	0.0394	"	1 hour	" "
3.....	0.0385	"	1 "	" "

No. 3 was evaporated to dryness after expelling bromine, redissolved in water slightly acid with hydrochloric acid, and filtered, the sulphur being determined in the filtrate. This, at least, shows that the higher results obtained on this sample were not due to any sulphur absorption from the flame. The use of potassium carbonate shows no decided gain in action or time.

To test the efficiency of the shield, several blank determinations were made with, and without, its use, and the following results obtained.

Three grams of the basic mixture were used and the ignition continued for one hour.

Nos.	Without shield.	With shield.
1.....	0.0025 gram $BaSO_4$ found	0.0025 gram $BaSO_4$ found
2.....	0.0024 " " "	0.0025 " " "
3.....	0.0025 " " "	0.0024 " " "
4.....	0.0026 " " "	0.0023 " " "

There is evidently no decided advantage in the use of the shield when gasoline gas is used, and care is exercised in igniting the mixture, the flame being kept away from the front or mouth of

the crucible. No. 4 of the above, without shield, was ignited so that the flame partly passed by the mouth of the crucible.

The writer is not able to state the value of the shield when ordinary gas is used, but at all events an alcohol lamp of good-sized flame may be safely used.

SAMPLE No. 2.

Evolution + residue.	HNO_3 and KClO$_3$.	Bamber's method.	Oxidation in presence of basic mixture.	Time of ignition.	Fineness of sample.	Mixture used.		Shield.
0.032	0.032	0.030	0.031	1 hour	60 mesh	MgO, K_2CO_3 & Na_2CO_3		No
0.032	0.030	0.031	0.031	45 min.	"	"	"	Yes
0.032	0.030		0.032	1 hour	"	"	"	Yes
....	0.032							

The sulphur was precipitated directly without any previous evaporation to dryness.

In samples Nos. 3 and 4 the sulphur has been determined by the following: 1. Booth, Garrett and Blair; 2. Cramer and Bicknell; 3. Andrew S. McCreath; 4. Albert W. Smith. In the following table their respective numbers are placed after their results.

SAMPLE No. 3.

Evolution + S in residue.	Chemist's number.	HNO_3 oxidation.	Chemist's number.	Bamber's method.	Chemist's number.	Oxidation in presence of basic mixture.	Fineness.	Time.	Shield.
0.066	1	0.075	2	0.076	1	0.077	60	1 hr.	Yes
....		0.075	3			0.076	60	½ hr.	No
....		0.076	4			0.076	60	1 hr.	No

SAMPLE No. 4.

Evolution method + residue.	Chemist's number.	HNO_3 oxidation.	Chemist's number.	Bamber's method.	Chemist's number.	Oxidation in the presence of basic mixture.	Fineness.	Time.	Shield.
0.043	1	0.058	2	0.054	1	0.054	80	1 hr.	No
....		0.055	3			0.057	60	1 hr.	Yes
....		0.058	4			0.056	60	1 hr.	Yes
....						0.043[1]	30	1 hr.	Yes

[1] Results obtained with 30-mesh sample clearly show an incomplete oxidation.

The above samples have all been gray irons. White iron it was thought, on account of its low silicon and absence of graphitic carbon, would not lend itself as readily to oxidation; but samples of white irons, treated in the same way, were oxidized as completely and in the same time as gray.

SAMPLE OF WHITE IRON.

	Per cent. sulphur.	Per cent. sulphur.	Per cent. sulphur.
Bamber's method.....	0.431	0.432	0.429
Oxidation in basic mixture ...	0.432	0.430	0.430

This method could no doubt be worked to advantage, using a stream of oxygen and combustion tube. The method does away with the precipitation of the sulphur in the presence of the ferric salt, and the time required for a determination is about that required for the determination of sulphur in coke.

LABORATORY OF THE E. & G. BROOKE IRON CO.,
BIRDSBORO, PA.

THE CONSTITUTION OF CAMPHENE.[1]

BY F. D. DODGE.

Received April 17, 1902.

THE constitution of camphene is as yet an unsettled point in the chemistry of the terpene series. The objections to the Bredt formula[2] have been stated by Semmler[3] and others, but no satisfactory substitute has been suggested.

As a result of some experiments with the reaction of Bertram and Walbaum,[4] the addition of acetic acid, in presence of mineral acids, I have been led to a somewhat different conception of the camphene molecule.

Camphene and pinene yield the acetates of isoborneol and terpineol, respectively. As regards other terpenes, but little appears to have been published, and I have made the following experiments.

1. *Pinene*, from American turpentine (sp. gr. 0.867. $\alpha_D = +11°$). 50 cc. with 100 cc. pure acetic acid, containing 1 per cent. sulphuric acid, allowed to stand at 15°-20° for five days. Quantitative saponification showed 43 per cent. terpineol acetate.

[1] Read before the New York Section of the American Chemical Society, February 7, 1902.

[2] *Ber. d. chem. Ges.*, (1893), p. 3056.

[3] *Ibid.*, (1900), p. 3421.

[4] *J. prakt. Chem.*, 49, 1.

2. *Camphene* (by Reychler's method from pinyl chloride), after six days, product contained 77 per cent. isobornyl acetate.

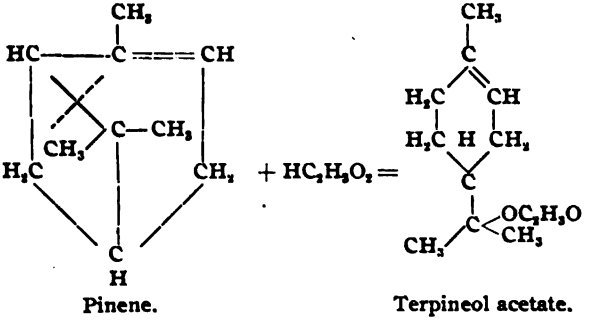
3. *Limonene* ($\alpha_D = +100°$. Sp. gr. $= 0.847$), after five days, $\alpha_D = 0°$, product showed 4 per cent. of acetate. On distillation, about 50 per cent. of a terpene mixture was obtained, containing principally terpinene.

4. *Terpinolene* (from terpineol by oxalic acid), after six days, 11 per cent. acetate formed.

5. *Terpinene* (from limonene), after six days, 8 per cent. acetate.

It is to be noted that the bornylene of Wagner, to which must probably be assigned the camphene formula of Bredt, also does not combine with acetic acid under these conditions, which fact was utilized by Wagner to separate it from camphene.[1]

Pinene and camphene are thus sharply differentiated from the other terpenes. The acetic reaction is not obtained (or but to a limited extent) with any singly or doubly unsaturated terpene, except in the case of pinene. But in pinene, the double bond is not attacked, but the 4-ring is opened, producing a terpineol derivative.



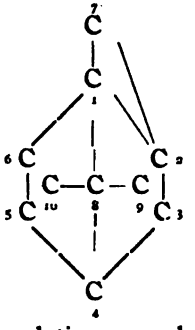
Pinene. Terpineol acetate.

The possibility now suggests itself, that in camphene we may have, not a double bond, but a 4-ring (or possibly a 3-ring) which is readily opened, yielding the ester of isoborneol.

The close relations of camphene, isoborneol, and camphor indicate with great probability that camphene contains the camphor nucleus, in which case there are but two possibilities of such additional ring-formation.

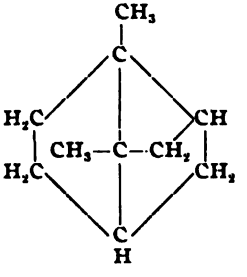
[1] *Ber. d. chem. Ges.*, (1900), p. 2121.

1. A 3-ring between C_1, C_2, and C_7.



A study of the spacial relations as shown by the tetrahedral models leads to the conclusion that such a structure is improbable. This assumption would also lead to a formula for camphenilone, which is identical with that established for the fenchocamphorone of Wallach.[1] These two compounds are, however, certainly not identical, and the C_1, C_2, C_7 ring hypothesis is hence untenable.

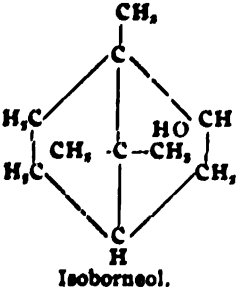
2. A 4-ring, C_1, C_2, C_9, C_8, leads to the formula



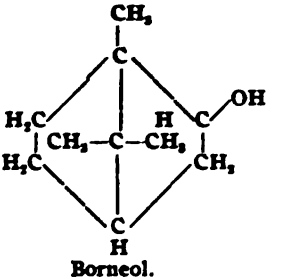
which, I believe, best explains the properties and reactions of camphene.

As in the case of pinene, we have here a 4-atom ring, readily opened under the influence of acids, yet differing from pinene in one respect. When the 4-ring of pinene is separated, the molecule is rearranged in more stable forms either of the terpineol or camphor series, and reversion to pinene is impossible. In camphene, the atoms composing the 4-ring are, as it were, held in position by the stable 5- and 6-ring nucleus, and the 4-ring may be opened and closed *ad libitum; i. e.*, we can pass from camphene to isoborneol, and the reverse at will. To isoborneol must be assigned the cis-configuration, while borneol is represented by the trans-form.

[1] *Ann. Chem.* (Liebig), **300**, 294; **302**, 371; **315**, 273.



Isoborneol.

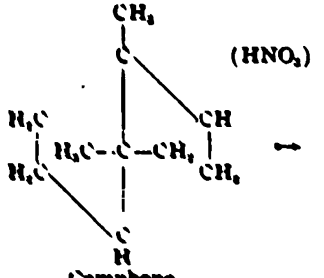


Borneol.

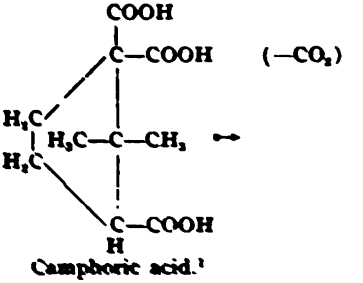
The greater reactivity of isoborneol is due to the proximity of the hydroxyl to the C_9 methyl group, and the differences in properties of the cis-chloride (isobornyl chloride, camphene hydrochloride) and the trans-chloride (bornyl chloride, pinyl chloride) are similarly explained.

According to this hypothesis, camphene is a saturated molecule, *i. e.*, contains no double bond. In fact there appears to be very little reason to consider it unsaturated. The difficult oxidation by permanganate, the action of bromine, etc., and many other reactions show that camphene is differently constituted from the typical unsaturated terpenes.

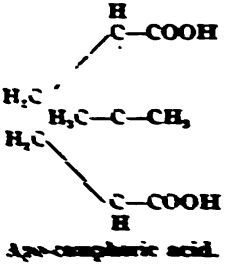
The new formula explains very satisfactorily the various oxidation products of camphene. Thus, we have:



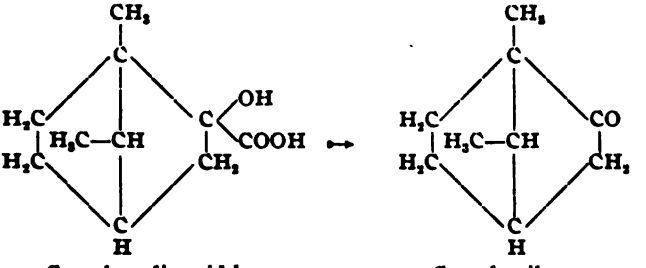
Camphene.



Camphoric acid.[1]

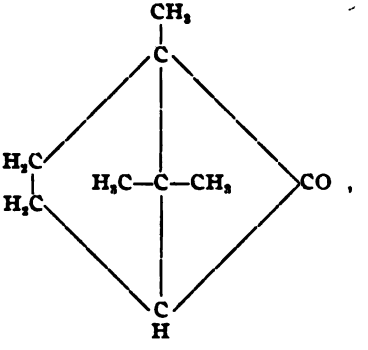


Apo-camphoric acid.

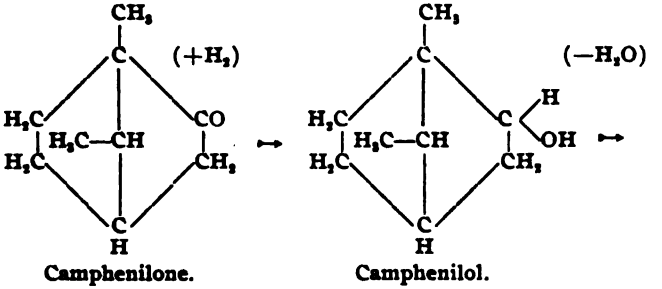


Camphenylic acid.[1] Camphenilone.

Camphenilone, $C_9H_{14}O$, here appears as a true lower homologue of camphor, which it strikingly resembles. Jagelki's formula,[2]

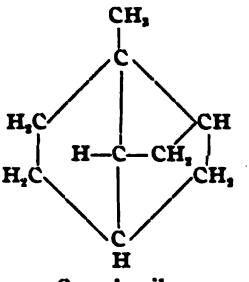


is improbable, because it assumes an oxidized 4-carbon ring, which is known to be an unstable arrangement, and it leads further to very improbable formulas for dehydrocamphenylic acid, and camphenilene. The new formula presents no serious difficulties. Thus:



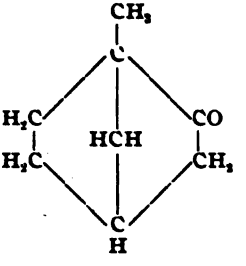
Camphenilone. Camphenilol.

[1] *Chem. Centrbl.*, (1897), I, p. 1056.
[2] *Ber. d. chem. Ges.*, (1899), p. 1498.

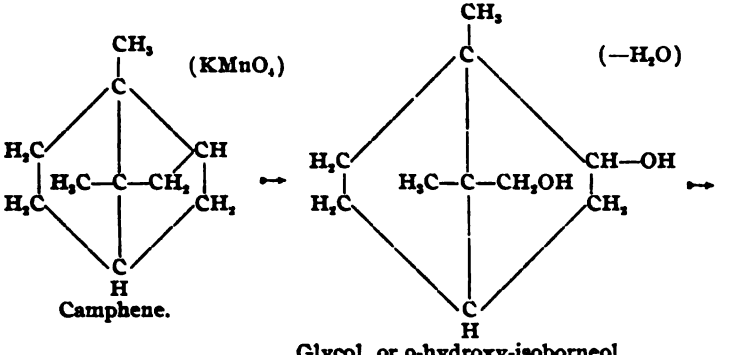


Camphenilene.

These reactions are exactly analogous to the formation of camphene from camphor, and if the hypothesis is correct, it should be possible to put camphenilene through further transformations, leading finally to the second lower homologue of camphor:



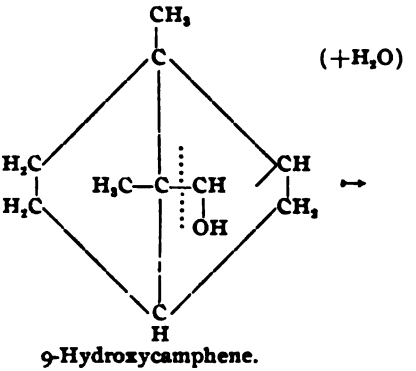
Wagner's camphene glycol[1] and its reactions may be shown as follows:



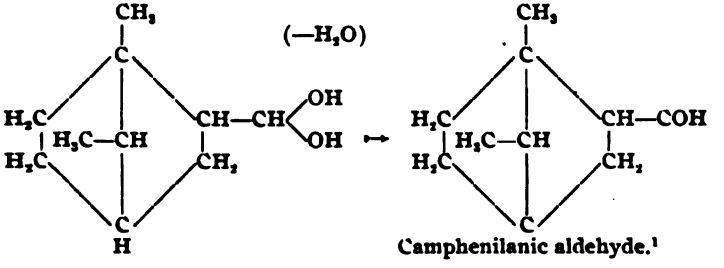
Camphene.

Glycol, or 9-hydroxy-isoborneol.

[1] *Ber. d. chem. Ges.*, (1890), p. 2311.



9-Hydroxycamphene.



Camphenilanic aldehyde.[1]

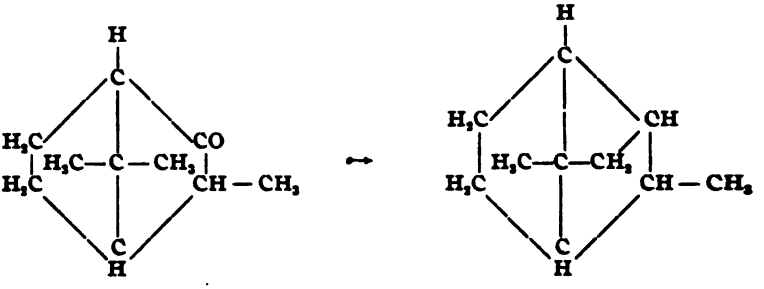
Further oxidation then leads to camphenilanic acid, camphenylic acid, and camphenilone.

As regards the other oxidation products mentioned by Jagelki (*l. c.*), it is unnecessary to discuss them in detail. Blaise,[2] who has examined and repeated some of Jagelki's work, arrives at rather different results. He concludes that the former's camphenilone formula cannot possibly be correct, and that this compound does not contain the trimethylcyclopentene ring characteristic of the camphor series. This deduction is entirely in harmony with the formulas here suggested.

A few other points in connection with the camphene formula remain to be mentioned.

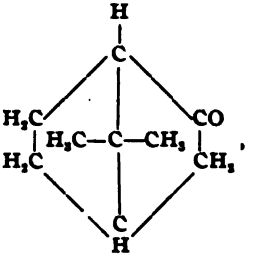
It has been shown[3] that fenchene behaves, with acetic acid, like camphene, and we are led to an analogous formula:

[1] *Chem. Ztg.*, (1896), p. 842. *Ber. d. chem. Ges.*, (1899), p. 1498.
[2] *Compt. rend.*, 129, 886.
[3] Schimmel & Co.: *Chem. Centrbl.*, (1898) II., p. 985.



Fenchone. Fenchene (?).

But, fenchocamphorone has, most probably, the structure,



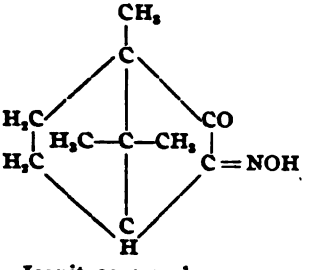
Fenchocamphorone.

and its formation from this fenchene is hard to explain. Wallach,[1] however, has recently shown that ordinary fenchene is a mixture of at least three compounds, and Kondakow and Lutschinin[2] have reached a similar conclusion. The conditions in the fenchone series appear to be complex, and further experiment is necessary.

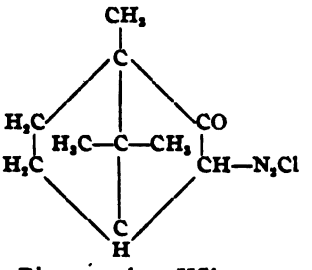
The characteristic feature of the new camphene formula is the connection between C_2 and C_9. Now the symmetry of the camphor nucleus shows that if such a connection is possible, a similar one may occur between C_3 and C_9.

In fact a compound is known, which I believe is best represented by such a formula. This is the camphenone of Angeli[3] whose formation may be shown thus:

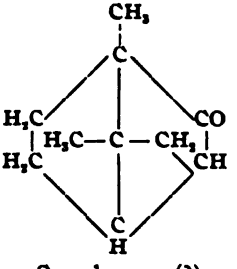
[1] *Ann. Chem.* (Liebig), **302**, 371; **315**, 273.
[2] *Chem. Ztg.*, **23**, 131.
[3] *Gazz. chim. ital.*, **23**, (II.) 351; **24**, (II.) 318.



Isonitrosocamphor.

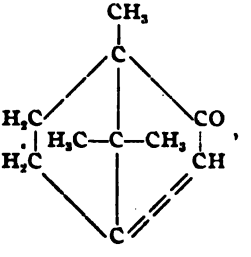


Diazocamphor, HCl.



Camphenone (?).

Angeli proposed the formula



but the tetrahedral models show that this structure is highly improbable. Harries and Matfus[1] have further found that camphenone does not show the hydroxylamine reaction characteristic of $\alpha\beta$-unsaturated ketones.

I would add, finally, that camphenilone, if correctly formulated above, should yield isonitroso and oxy-methylene derivatives, which are improbable if Jagelki's formula is true. These reactions are under investigation.

NEW YORK, February, 1902.

[1] *Ber. d. chem. Ges.*, **32**, 1340.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

DETERMINATION OF SULPHURIC ACID IN SOILS.

BY C. B. WILLIAMS.

Received March 13, 1902.

SULPHUR generally occurs in the soil in the form of sulphates and has been heretofore estimated by slightly acidifying the soil solution with hydrochloric acid, boiling and then precipitating by slowly adding barium chloride with constant stirring. After standing a few hours, the precipitate is filtered, washed, dried and weighed as barium sulphate and calculated to sulphur trioxide.

There are three difficulties generally encountered in determining sulphuric acid in soils: (1) The small quantity of the constituent usually present; (2) the solubility of some of the barium sulphate precipitate in the ferric chloride or aluminum chloride or both, which are almost invariably present; (3) as well as on the other hand the strong liability of the precipitate becoming contaminated by iron, especially if the soil is of a ferruginous character and the soil solution is not strongly acid.

Lunge[1] found that in determining sulphur in pyrites unless the solution is strongly acidulated with hydrochloric acid, considerable iron is carried down with the barium sulphate and is not removed by washing; on the other hand he found that the barium sulphate is dissolved by the solution if too strongly acid. Experiments by Jannasch and Richards[2] show that if sulphuric acid is precipitated in the presence of iron, a double barium iron sulphate is formed which, when ignited, sets free sulphur trioxide. They, in the light of their work, stated that to obtain correct results the iron had to be removed before precipitation with barium chloride.

The conditions and difficulties cited above are similar to those that frequently obtain when we come to determine sulphur in soils, for not infrequently soils contain as much as 5 to 15 per cent of ferric oxide. Now if Lunge found it difficult to estimate sulphur with any degree of accuracy in the presence of iron in pyrites, then may we not expect to encounter difficulty when we attempt to estimate it in soils where the relative proportion of iron

[1] *Ztschr. anal. Chem.*, 19, 419-431.

[2] *J. prakt. Chem.*, 39, 321.

to sulphur is vastly greater and the sulphur usually in such minute quantities as to require the greatest precision without unfavorable conditions?

The writer in analyzing soils during the past year noticed that if iron and alumina were first removed by precipitation with ammonia, the results were considerably higher in almost all instances than if the acid was precipitated direct as directed in the methods prescribed by the Association of Official Agricultural Chemists. It was also observed that the precipitate was coarse-grained and did not tend to run through the filter as it did if precipitated in the presence of iron and alumina.

In the following table are recorded comparative results obtained by the two methods, or rather two modifications of the same method. Those under "official" are obtained by the method prescribed by the Association of Official Agricultural Chemists, while those under "modified" are results obtained by first removing the iron and alumina before precipitating the barium sulphate.

	Per cent. sulphur trioxide.		
Soil No.	Official method.	Modified method.	Difference.
58	0.013	0.040	0.027
59	0.019	0.037	0.018
60	0.022	0.034	0.012
61	0.015	0.036	0.021
62	0.012	0.031	0.019
63	0.039*	0.039	
64	0.020	0.040	0.020
65	0.015	0.032	0.017
66	0.011	0.030	0.019
67	0.050	0.061	0.011
68	0.013	0.029	0.016
70	0.057	0.065	0.008
71	0.027	0.041	0.014
72	0.026	0.031	0.005
73	0.017	0.027	0.010
74	0.022	0.038	0.016
75	0.021	0.031	0.010
76	0.026	0.041	0.015
77	0.034*	0.034	
78	0.110*	0.106	
79	0.021*	0.031	
80	0.103	0.123	0.020
81	0.087*	0.106	
82	0.027	0.055	0.028
83	0.058*	0.050	

* Barium sulphate colored brown by the presence of iron.

Soil No.	Per cent. sulphur trioxide. Official method.	Modified method.	Difference.
84	0.065	0.098	0.033
85	0.034	0.087	0.053
86	0.007	0.082	0.075
87	0.003	0.045	0.042
88	0.024	0.057	0.033
89	0.000	0.050	0.050
90	0.082	0.093	0.011
91	0.017	0.046	0.029
92	0.041	0.058	0.017
93	0.027	0.034	0.007

In the first eleven results by both methods, 4 grams of soil were taken for the determinations, in the next twelve, 2 grams for the "official" and 1 gram for the "modified," and in the last twelve 1 gram for the "official" and 2 grams for the "modified" methods. It is seen that the differences generally with the last twelve soils by the two methods are much greater than in the preceding twenty-three. The explanation for this greater divergence seems to lie in the amount of soil taken for analysis, as all other conditions were identical and it is noticed that when only 1 gram of soil is used with the "official" method the sulphuric acid is precipitated in such a finely divided condition that a little will pass the most retentive filter-paper (No. 589, S & S, blue ribbon) unobserved, unless the filtrate is examined very closely by transmitted light.

Whatever else may be said, the results in the table point very clearly to the fact that when sulphuric acid is precipitated in the presence of iron and alumina some of the barium sulphate is dissolved by either the ferric chloride or aluminum chloride or by both, and that it can only be determined accurately in soil solutions in which these two bases have been eliminated. If the results by the "modified" method are correct, and it can not be seen why they are not, as the ferric and aluminum hydroxides were in all instances washed at least ten times, using about 20 cc. at each washing, then the "official" method lacks over 35 per cent. of getting out all the sulphur trioxide in the above thirty-five samples.

In an experiment to test the solubility of barium sulphate in ferric chloride, it was found that when a solution was taken containing 0.110398 gram ferric chloride and 0.001288 gram of sulphuric acid (the averages of both sulphur trioxide and ferric chloride in the thirty-five samples experimented with when 2 grams of

soil are taken), that 17 per cent. of the sulphur trioxide was dissolved, results being obtained in closely agreeing duplicates. In a preliminary experiment it was observed that if the solution was only slightly acid (0.2 cc. excess of concentrated hydrochloric acid) iron in some form, probably an oxychloride, was frequently deposited on the bottom of the beaker in boiling prior to the addition of barium chloride, and stuck so tenaciously as to be removed only by the addition of considerably more hydrochloric acid. This same phenomenon was often observed in working with soils containing a moderately high percentage of iron with only a slight acidity of the soil solution.

In the experiment above to ascertain the solubility of barium sulphate in ferric chloride, 3 cc. excess of hydrochloric acid were present, as this was sufficient to prevent the deposition of iron and was found in a preliminary trial to exert an inappreciable, if any, dissolving effect.

Although the determination of sulphuric acid is not at present considered by soil chemists of the highest importance, because it generally exists in most soils in sufficient quantity for the complete development of crops for years to come, yet its importance as an essential constituent of plant food and its probable deficiency in many instances has prompted the writer to submit the above results and observations.

THE INTERACTION OF SULPHURETTED HYDROGEN AND ARSENIC ACID.[1]

BY L. W. MCCAY.

Received March 31, 1900.

FROM solutions of arsenic acid which have been treated with sulphuretted hydrogen I have been able to separate large amounts of monosulphoxyarsenic acid in the form of its tertiary sodium salt, and small amounts of disulphoxyarsenic acid, also in the form of its tertiary sodium salt. In addition to the above-mentioned acids the solutions appear to contain some trisulphoxyarsenic acid. Thus far, however, all attempts to isolate this compound have failed. If we assume its existence in the solutions, and a number of facts warrant us in making the assumption, the action of

[1] The facts given in the first part of this article have been taken from a paper which appeared in the *Ztschr. anorg. Chem.*, 29, 36 (1901).

sulphuretted hydrogen upon arsenic acid would appear to be in harmony with Ostwald's law of successive reactions (Gesetz der Reactionsstufen). The successive stages through which arsenic acid passes during its transformation into sulpharsenic acid would then find expression in the following equations:

I. The sulphuretted hydrogen is always present in large excess.

$$1.\ H_3AsO_4 + H_2S = H_3AsO_3S + H_2O$$
$$2.\ H_3AsO_3S + H_2S = H_3AsO_2S_2 + H_2O$$
$$3.\ H_3AsO_2S_2 + H_2S = H_3AsOS_3 + H_2O$$
$$4.\ H_3AsOS_3 + H_2S = H_3AsS_4 + H_2O$$

Since sulpharsenic acid cannot exist in the free state we have:

$$2H_3AsS_4 = As_2S_5 + 3H_2S.$$

The sulphoxyarsenic acids, however, are unstable compounds and when the sulphuretted hydrogen is present in the solutions in but small amounts they break down partially, the monosulphoxyarsenic acid into arsenious acid and sulphur, the disulphoxyarsenic acid into arsenious acid, sulphur and the sulphides of arsenic. The sulphuretted hydrogen then converts the arsenious acid into arsenic trisulphide. Some arsenic pentasulphide is also formed according to I. We'll have then:

II. The current of sulphuretted hydrogen is slow or intermittent, so that the gas is not continually in excess:

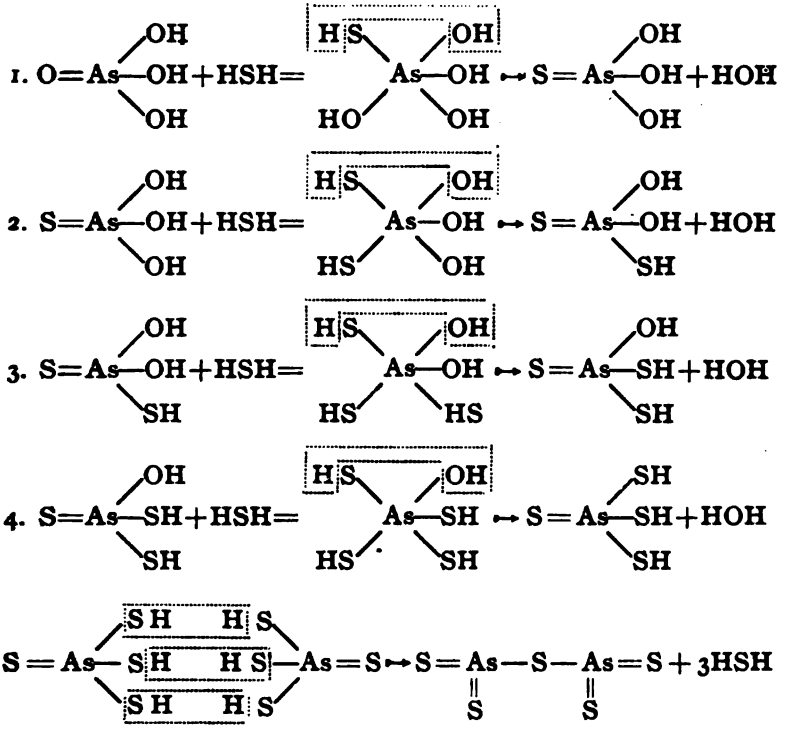
$$1.\ H_3AsO_4 + H_2S = H_3AsO_3S + H_2O$$
$$2.\ 2H_3AsO_3S = 2H_3AsO_3 + 2S$$
$$3.\ 2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$$
$$4.\ H_3AsO_3S + H_2S = H_3AsO_2S_2 + H_2O$$
$$5.\ 6H_3AsO_2S_2 = As_2S_5 + As_2S_3 + 4S + 2H_3AsO_3 + 6H_2O$$
$$6.\ 2H_3AsO_2S_2 + H_2S = As_2S_5 + 4H_2O, \text{ etc.}$$

When, therefore, in these circumstances, the arsenic is all down, the precipitate will consist of a mechanical mixture of arsenic pentasulphide, arsenic trisulphide and sulphur, and this is in accordance with the facts.

The changes which occur when sulphuretted hydrogen acts on arsenic acid remind us forcibly of the reactions of organic chemistry. Are the former analogous to esterifications,[1] or are they

[1] $R.OH + CH_3.\overset{\overset{O}{\|}}{C}-OH = CH_3.\overset{\overset{OR}{/}}{C}-\underset{\underset{OH}{|}}{O}H \rightarrowtail CH_3.\overset{\overset{O}{\|}}{C}-OR + HOH.$

true ionic reactions? I firmly believe that they are ionic reactions, not simple but complex ionic reactions. However, to settle the matter beyond a doubt we need more facts. If the changes are additions and splittings, the mechanism of the various steps can be represented by the following equations:



Let us now endeavor to see if the electrolytic dissociation theory can be applied to an interpretation of the reactions.

The various hydrogen atoms of a polybasic acid have different values as regards the strength of the latter. The first atom of hydrogen in a molecule of such an acid is always that of a stronger acid than the second, while the third and fourth follow in the same order. The first step in the dissociation of a polybasic acid is the most important one, and the amount of this dissociation depends upon the relative strength of the acid. Now since arsenic acid is a weak acid,[1] the dissociation which it undergoes when we dissolve

[1] According to Walden's measurements, it is about 20 per cent. dissociated in 01. molar sol.

it in water will be necessarily small, so that the second and third steps in the breaking-down of the molecule can be neglected:

$$H_3AsO_4 \rightleftharpoons H_2AsO'_4 + H^{\cdot}$$

But since arsenic exhibits basic as well as acid properties, it seems reasonable to assume that arsenic acid can also undergo a slight basic dissociation. What has just been said in regard to the dissociation of a polybasic acid is correspondingly true of a polyacid base. The first step in the dissociation is the important one and since arsenic acid, if looked upon as a base, is undoubtedly a very weak one, the second and third stages in the cleavage of the molecule can be disregarded. The basic dissociation of the compound would be represented thus:

$$H_3AsO_4 \rightleftharpoons H_2AsO^{\cdot}_3 + OH'.$$

We may indicate both dissociations in this way:

$$OH' + H_2AsO^{\cdot}_3 \rightleftharpoons H_3AsO_4 \rightleftharpoons H_2AsO'_4 + H^{\cdot}.$$

The foregoing equation represents then, the equilibrium existing in an aqueous solution of arsenic acid. The $C_{(OH')}$ is extremely small, less even than the $C_{(OH')}$ in water, because, in general,

$$C_{(H^{\cdot})} \times C_{(OH')} = K$$

and if we increase the $C_{(H^{\cdot})}$ the $C_{(OH')}$ will correspondingly decrease. An aqueous solution of arsenic acid has a far greater value of $C_{(H^{\cdot})}$ than pure water, and hence a much less value of $C_{(OH')}$.

Again, consider the expression

$$C_{(OH')} \times C_{(H_2AsO_3^{\cdot})} = K_1 \times C_{(H_3AsO_4)}.$$

Here the numerical value of K_1 is, of course, unknown, but even though it is undoubtedly very small, the value of $C_{(H_2AsO_3^{\cdot})}$ may still be appreciable, since the value of $C_{(OH')}$ is kept so extremely low by the considerable concentration of the $H^{\cdot}$ ions.

Allow the solution to be saturated and *kept* saturated with sulphuretted hydrogen.

$$H_2S \rightleftharpoons H^{\cdot} + SH'.$$

The degree of dissociation is slight, for sulphuretted hydrogen is a very weak acid. The dissociation, too, will be depressed to some extent by the hydrogen ions of the arsenic acid, seeing that arsenic acid is a stronger acid than sulphuretted hydrogen. It is

plain, however, that the $C_{(OH')}$ in the solution will be far less than the $C_{(SH')}$.

If, now, some SH′ ions and some $H_2AsO'_3$ ions unite, some undissociated monosulphoxyarsenic acid will be formed, the equilibrium of the system will be disturbed, more $H_2AsO'_3$ ions will appear and more monosulphoxyarsenic acid will come into existence. In spite, therefore, of the very small value of $C_{(H_2AsO'_3)}$ at the moment when the sulphuretted hydrogen is introduced into the solution, the resulting $C_{(SH')}$ value will soon become sufficiently great to occasion the production of a measurable amount of monosulphoxyarsenic acid,

$$H_2AsO'_3 + SH' = H_2AsO_2S.$$

Monosulphoxyarsenic acid is capable of undergoing two kinds of basic dissociation:

$$1.\ H_2AsO_2S \rightleftharpoons SH' + H_2AsO'_3$$

and

$$2.\ H_2AsO_2S \rightleftharpoons OH' + H_2AsO_2S'.$$

Since the SH′ ions are far in excess of the OH′ ions, the second kind of dissociation would probably predominate and since the solution is kept saturated with sulphuretted hydrogen, some H_2AsO_2S' ions will combine with SH′ ions and some undissociated disulphoxyarsenic acid will be produced. The disulphoxyarsenic acid will, in its turn, yield $H_2AsOS'_3$ and OH′ ions, and $H_2AsOS'_3$ and SH′ will unite to form some trisulphoxyarsenic acid, and so on to the end.

The small ionic concentrations and the appearance and disappearance of the complex ions are quite in harmony with the sluggishness of the reactions, and a consideration of the rates of the various transformations would indicate the existence, at some time during the interactions, of a considerable concentration of monosulphoxyarsenic acid; later the maximum concentration of the disulphoxyarsenic acid, which, however, would be less than the maximum concentration of the former, and later still the maximum concentration of the trisulphoxy-compound, which indications are in accordance with the facts.

Now Brauner and Tomicek,[1] as well as Neher,[2] have shown that strong acids (HCl and H_2SO_4) accelerate, in a most pronounced way, the transformation of arsenic acid by means of sulphuretted hydrogen into sulpharsenic acid, so the question at once arises,

[1] *J. Chem. Soc.*, **33**, 145.
[2] *Ztschr. anal. Chem.*, **32**, 45.

What role do these strong acids play? In the light of what I have already said it is evident that the increase in the value of $C_{(H')}$, due to the presence of such acids, serves to decrease the value of $C_{(OH')}$ and so promotes the basic dissociation of the arsenic acid. These strong acids will, of course, lower the dissociation of the sulphuretted hydrogen, but we must remember that while the value of $C_{(SH')}$ undoubtedly falls off, that of $C_{(OH')}$ is reduced in a vastly greater proportion.

Given then an aqueous solution of arsenic acid, saturated and kept saturated with sulphuretted hydrogen, or given an aqueous solution of arsenic acid containing a considerable amount of a strong mineral acid (HCl) and saturated and kept saturated with sulphuretted hydrogen, and omitting any consideration of the second and third steps in the basic dissociation, we may represent the successive reactions in the following way:

1. $H_3AsO_4 \rightleftharpoons H_2AsO'_4 + OH'$
2. $H_2AsO'_4 + SH' = H_3AsO_3S$[1]
3. $H_3AsO_3S \rightleftharpoons H_2AsO_2S' + OH'$
4. $H_2AsO_2S + SH' = H_3AsO_2S_2$
5. $H_3AsO_2S_2 \rightleftharpoons H_2AsOS'_2 + OH'$
6. $H_2AsOS'_2 + SH' = H_3AsOS_3$
7. $H_3AsOS_3 \rightleftharpoons H_2AsS'_3 + OH'$
8. $H_2AsS'_3 + SH' = H_3AsS_4$

The sulpharsenic acid then breaks down:

$$2H_3AsS_4 = As_2S_5 + 3H_2S.$$

Neher[1] observed a number of years ago, and his results have been confirmed by Weinland[2] and myself,[3] that when arsenic acid is present in a mixture of two volumes of strongest aqueous hydrochloric acid and one volume of water, sulphuretted hydrogen precipitates the arsenic almost instantly as the pentasulphide. If

[1] Since the structural formula for monosulphoxyarsenic acid is undoubtedly $S = As(OH)_3$, it would, perhaps, be more rational to assume, in the solution, the presence of the normal compound $As(OH)_5$.

$$As(OH)_5 \rightleftharpoons As(OH)'_4 + OH'$$

$$As(OH)'_4 + SH' = As(OH)_3S \longleftrightarrow S = As(OH)_3 + HOH, \text{ etc.}$$

[2] *Ztschr. anal. Chem.*, 32, 45.

[3] *Ztschr. anorg. Chem.*, 14, 44.

the rapid formation of the pentasulphide is in this case due to the $C_{(H^+)}$ then any strong acid which would give as great a $C_{(H^+)}$ as hydrochloric acid should have a similar effect, providing, of course, the anions occasion no disturbing by-reactions. Neher tried sulphuric acid and found that it acted in a manner analogous to hydrochloric acid. Nitric acid must be excluded but the behavior of other strong acids would prove interesting. There is, however, another way of looking at the matter. Assuming, as we have done, that arsenic acid can act as a very weak base, in the presence of a great excess of such a strong acid as hydrochloric acid, the production of the salt arsenic pentachloride[1] is at least not impossible. It would doubtlessly be formed by stages but the final product of the reaction we may assume to be the pentachloride:

$$AsCl_5 \rightleftharpoons As^{\cdot\cdot\cdot} + 5Cl$$

$$2As^{\cdot\cdot\cdot} + 10SH' = 2H_3AsS_4 + 2H_2S \rightarrowtail As_2S_5 + 5H_2S.$$

If the train of reasoning above given be correct, the facts cited in my paper in the *Zeitschrift für anorganische Chemie* find a very satisfactory explanation in terms of the electrolytic dissociation theory.

In closing I wish to express my sincere thanks to Dr. George A. Hulett, of the University of Michigan, for his kindness in suggesting to me the possibility of arsenic acid undergoing a slight basic dissociation, as well as for the friendly interest he has shown in my work.

PRINCETON, N. J., February 1, 1902.

THE SOLUBILITY OF GYPSUM.

BY GEORGE A. HULETT AND LUCIUS E. ALLEN.

Received April 2, 1902.

ALTHOUGH the solubility of the substance $CaSO_4.2H_2O$ has been the subject of investigation by many careful workers, the results vary widely, while the experimental errors are comparatively small. The cause of these discrepancies was pointed out by Hulett,[2] in the course of an investigation of the influence of

[1] In this case we would have to assume that the aqueous solution of arsenic acid contains the normal compound H_3AsO_4.

[2] *Ztschr. phys. Chem.*, **37**, 385.

surface-tension on solubility, where it was shown that the energy existing on the surface between a solid and its saturated solution is a measurable factor of the solubility. The concentration of the solution in equilibrium with a curved surface is different from that in equilibrium with a plane surface. Attention was called to a *normally saturated solution; i. e.*, the solution which is in equilibrium with a plane surface of the solid, and it was shown that a convex surface will show greater solubility and a concave one a less solubility than a plane surface; *e. g.*, if the solid is finely divided the solubility will be noticeably greater; in the case of gypsum[1] the solubility was increased 20 per cent. by decreasing the size of the particles to 0.3 micron. When larger pieces of gypsum were placed in a flask with water and rotated in a thermostat—the usual method of saturating a solution—the concentration became 5 per cent. greater than a normally saturated solution at the same temperature, because gypsum is a very soft mineral and is easily ground to powder. It was therefore found necessary to remove all the small particles and then cause the liquid to rotate over the solid, but without disturbing it.

At 25° a normally saturated solution of gypsum contained 15.33 milligram-molecules in a liter (a supersaturated solution was stirred in contact with the gypsum plates at 25° C. and decreased in concentration to 15.33 milligram-molecules to a liter, leaving no doubt as to the question of equilibrium having been established). All previous determinations of the solubility of gypsum vary more or less from the above figure for 25° C., and the results are greater than 15.33 milligram-molecules in a liter, indicating that where care had been taken to avoid supersaturation, the solutions analyzed were still those in equilibrium with more or less convex surfaces, due to the fact that too finely divided gypsum had been used. In view of the above facts and the special importance of the solubility curve of gypsum, a careful determination of the concentrations of normally saturated solutions of gypsum was undertaken.

SOLUBILITY IN GENERAL.

The question as to how solubility should be expressed has received very little attention and with the numerous methods in vogue there is little uniformity in the published results. The densities of

[1] *Zeitschr. phys. Chem.*, 37, 368.

the solutions worked with are seldom given and the lack of these data often excludes comparisons or recalculations. In the case of a slightly soluble substance like gypsum (2.4 grams per liter) the results are mostly given as parts of water to dissolve 1 part of gypsum, while from the context it appears that the calcium sulphate was determined from a volume of the solution. The question of the density of the solutions is not mentioned so the results are in reality volumes of solution which contain 1 gram of calcium sulphate, or gypsum, as the case may be. The error is not negligible and increases with the temperature.

If a quantity of the solution is weighed out in a weighing bottle[1] and the solute (the dissolved substance) is determined gravimetrically, the results are very definite as far as the masses of the solvent and the solute are concerned and the results are to be expressed as parts of solute to 100 parts of solution, or parts of solvent for 1 part of solute, or better still as gram-molecules dissolved by 100 gram-molecules of solvent, but the density is still needed as a control and to allow of comparison with results determined from volume. The results expressed as parts of solute to 100 parts of solution yield for the temperature curve nearly straight lines,[2] but not in all cases, and while there may be some advantage in locating a break or the appearance of a new phase when the curves are straight lines, still there is so little known at present concerning the relation of solubility to other magnitudes that this choice would be quite arbitrary.

A pipette is an exceedingly accurate instrument if graduated *to volume* (not grams water weighed in air), and the contents rinsed out. The volume taken is thus diluted by the rinsing water but the mass of the solute is determined gravimetrically. If the pipette is provided with a ground glass cap for the lower end, it serves at the same time as a pycnometer, or a good-sized pycnometer may be used for a pipette, first determining the density then washing out the solution and determining the solute analytically. In this manner not only the weight of the solution and solute are obtained but also the volume of the solution and the results can be expressed as gram-molecules of the solute in a liter, or in any manner desired. Since from the modern standpoint the dissolved substance is regarded as a gas,

[1] Van't Hoff: Vorlesungen, p 24.
[2] Etard: *Compt. rend.*, 108, 176.

there is much to be said in favor of expressing the solubility results as concentration or gram-molecules in a liter of the solution. A knowledge of the vapor-pressure of the solution is also very desirable as it allows of a calculation of the osmotic pressure and the application of other thermodynamic relations. With electrolytes conductivity is also expressed in terms of concentration, while solutions for volumetric analysis, with which all chemists are familiar, consider only the volume and mass of the solute. Complete data would include a determination of the mass, volume, and concentration of the normally saturated solution; the conductivity, if electrolyte, should be taken as a control and also, if possible, the vapor-tension.

THERMOSTATS.

For temperatures below that of the surroundings, there seems to be no satisfactory device for accurately controlling the temperature. In using the ordinary Ostwald regulator and a cooling tube in the bath, a good deal of tap water is required. This is due to the effect of the small flame, which continually burns beneath the bath. If we do away with this flame and have the bath well covered with felt and the top protected by glass and felt, then a very little ice-water from a convenient tank will keep the temperature down. A short coil of very fine platinum wire is arranged above the mouth of the regulator burner and by means of the second hand of a clock, which makes and breaks an electric current, this platinum wire is made to glow an instant every minute; now the regulator can shut the gas off entirely and when let on again the platinum which glows once every minute will light it. With our large 45-liter bath well protected with felt, the temperature can be maintained quite as accurately below as above room temperature and with very little ice-water dropping into the bath.

The thermostat used at zero consisted of a large tank of 45 liters' capacity, filled with fine cracked ice. The Bunsen flask used for solution was sunk into the ice and stood on a tripod. The bath was covered on all sides with a thick layer of felt and the ice kept for fully twenty-four hours without replenishing, the temperature remaining almost absolutely constant.

For all temperatures above room temperature, except at 100° C., a large bath was used which was covered on the sides with

several thicknesses of asbestos, the bottom being also covered, with the exception of a small circular place in the center for the flame, and the top was covered with glass plates and asbestos. The thermostat was let into a table so that it projected about 10 cm. above the top. Below, and extending from the table to the floor, four large sheets of asbestos enclosed the lower part of the bath, thus preventing draughts, etc., from effecting the temperature. This bath enabled us to keep within 0.1° even at 75°.

Jena flasks, Erlenmeyer form, were used, the flask being immersed to the neck in the bath and covered so that there was no distillation and condensation in the neck. The temperature was controlled to within 0.1 or 0.05 of a degree during saturation. A Shultz stirrer was used in the flask and the height of the stirrer was so regulated that the arms did not disturb the gypsum plates, but kept the solution in a slow but steady motion over them, the stirrer running about 50 revolutions per minute.

The bath used for 100° C. was much smaller than those used for the other temperatures, being of about 7 liters' capacity. The bath was filled about a third full of water so that the flask was not immersed in the boiling water, but was completely surrounded with steam. A long-necked Florence flask (Jena) was used and to prevent evaporation, a test-tube which fitted nicely into the neck of the flask, was provided with a short tube below for the passage of the stirrer-rod; the stirrer-rod was supported also by the cork in the upper part of the test-tube. The flask was thus closed off at the point where the neck joined the flask and was so full of water that there was little free surface for evaporation; this scheme effectually prevented distillation from the solution even at 100°.

All density determinations were made with a Sprengel-Ostwald pycnometer, capacity 25 cm^3. The end of the capillary arm of this pycnometer was provided with a ground-on cap to prevent loss by evaporation or in handling. As a control, the density of water was determined at the temperature of the experiment, and then the gypsum solution, under exactly the same conditions. The results were calculated to weight in vacuum and from the known density of water, the density of the solution was calculated to $\frac{mass}{cm^3}$, that is, referred to water at 4° C. Duplicates agreed to the fifth decimal place, leaving the sixth uncertain.

ANALYTICAL METHODS.

The analytical results were based on the amount of anhydrous calcium sulphate in 100 cm^3 (volume) of the gypsum solution saturated at a given temperature. The samples for analysis were taken from the solution flask while still immersed in the constant water-bath, by filling an accurately standardized 100 cm^3 (volume) pipette and at once allowing the solution to run into a weighed platinum dish, thoroughly rinsing the pipette with distilled water. The duplicate samples were then evaporated to dryness on water-baths, using condensing funnels to exclude dust. When evaporated to dryness the platinum dishes were placed in a specially constructed glowing oven, made as follows: A cylindrical sheet-iron or tin jacket was covered with asbestos, the seams of the asbestos being cemented together with a little sodium silicate. A conical cover was made, covered in the same manner, and having a small hole in the apex to allow of the escape of the gases of combustion. Within the jacket and about in the center was supported a casserole in which the platinum dish was placed, standing on three small pieces of porcelain. The casserole was then covered with an inverted evaporating dish. The whole apparatus was supported on a ring stand and heated from underneath with a Detroit burner. In this way the samples of gypsum could be carefully heated and the temperature within the casserole was sufficient to completely dehydrate the gypsum, but too low to decompose the calcium sulphate as the following experiment showed.

A known weight, 0.8788 gram, of the gypsum plates were placed in a weighed platinum dish and put in the glowing oven. After glowing for one and three-quarter hours, the platinum dish was cooled and weighed, giving the following weight—51.5600 grams; the dish was replaced in the oven and glowed for two hours under the same conditions and again cooled and weighed, giving the same weight as before—51.5600 grams. The loss of water was within 0.1 per cent. of the theoretical. It was noticed that the weight of the calcium sulphate would increase if left for a little time in the air; hence, it seems to be slightly hygroscopic and the weighings were made *rapidly*. The first heating gave the approximate weight and, having this, the second and following heatings could be done so rapidly that the error was entirely negligible. The residue of the above experiment was digested with a

little water but showed no suggestion of an alkaline reaction, while the weight indicated that it had not lost sulphur trioxide, nor did it lose weight on continued heating.

The gypsum used in this work was the same as that used in the previous work on gypsum.[1] It was from a very large and perfectly clear crystal from Wyoming. Analysis of a saturated solution of this gypsum showed no trace of chlorine. The gypsum was broken up into thin plates of 1.0 to 0.5 mm. thickness, and all fine particles were removed by repeated washing and decantation with distilled water. The water used was obtained by redistilling distilled water after addition of barium hydroxide,[2] only water having a conductivity of less than 1.5×10^{-6} being used for the solution of the gypsum. The capacity of the cells used in this work was determined by a N/50 potassium chloride solution, using the above water and carefully purified and fused potassium chloride. The results represent the conductivity of a cubic centimeter of the solution compared to a solution, 1 cc. of which has a resistance at the temperature of 1 ohm (106.3 $\frac{cm.}{mm.^2}$ Hg at 0°) (Kohlrausch unit).

The following table (I) gives the results obtained in this investigation; column II gives the actual weights, in duplicate, of the calcium sulphate (heated to constant weight as above described) from 100 cm^3 of the solution measured at the temperature of the experiment. Column III gives the calculated milligram-molecules in a liter at the temperature of the experiment. The result for 107°, 11.39 milligram-molecules in a liter, is exterpolated, and the course of the curve I (Fig. I) is so uniform that this figure is probably correct to the first decimal place. This point is the end of the gypsum curve since van't Hoff and Armstrong[3] have shown that at this temperature the vapor-pressure of gypsum equals that of water and (since the vapor-pressure of the gypsum solution varies so slightly from that of water) this is the temperature at which gypsum turns to halfhydrate. At 107°, under normal conditions, there is a break in the curve, and the continuation is the curve which is in equilibrium with $CaSO_4.\frac{1}{2}H_2O$.

Column IV gives the density $\frac{mass}{cm^3}$ at the temperature of the experiment; these data allow of a recalculation of the concentra-

[1] *Loc. cit.*

[2] Hulett: *Ztschr. phys. Chem.*, 33, 297.

[3] *Sitz. Ber.*, (1900), p. 559.

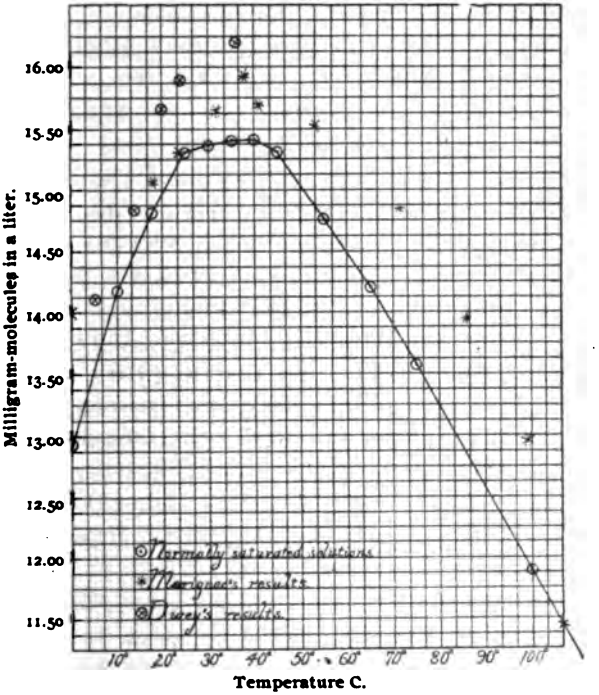
TABLE I.

I. Temperature.	II. Grams $CaSO_4$ in 100 cm^3 solution. Duplicate.	III. Millimolecules for 1 liter.	IV. Density of solution. Mass in $\frac{gm.}{cm^3}$. For T° C.	V. λ for T° C.	VI. λ for 25° C.	VII. Time for conductivity to become constant. Minutes.
0°	{0.1760 / 0.1758}	12.926	1.001970	0.000945	0.001958	..
10°	{0.1931 / 0.1926}	14.177	1.001727	0.001486	0.002080	90
18°	{0.2017 / 0.2015}	14.817	1.000590	0.001830	...	80
25°	{0.2083 / 0.2078}	15.295	0.999109	0.002206	0.002206	75
30°	{0.2092 / 0.2089}	15.361	0.997891	0.002445	...	60
35°	{0.2096 / 0.2096}	15.405	0.996122	0.00268	0.002226	50
40°	{0.2097 / 0.2097}	15.413	0.99439	0.002845	0.002232	45
45°	{0.2086 / 0.2081}	15.310	0.992370	0.003045	0.002264	60
55°	{0.2012 / 0.2007}	14.765	0.98796	0.003375	...	40
65.3	{0.1934 / 0.1930}	14.200	0.98256	0.003603	...	45
75°	{0.1851 / 0.1844}	13.575	0.977724	...	...	40
100°	{0.1624 / 0.1615}	11.900	...	...	...	..
107°	...	(11.390)	...	...	...	..

tion to any other standard. The weights are all corrected to vacuum. The densities differ rather uniformly from water by + 0.002. At 25° C. for example, from the density and the mass of solute (regarding it as calcium sulphate and specific gravity 3), we find the density of the solvent slightly greater than water (0.99773) instead of (0.99710), that is, the condensation of the solvent is very slight, only 0.00063.

Columns V and VI give the electrical conductivity in the standard unit. These were taken primarily to determine when the solution was saturated. Into a 1½ liter Erlenmeyer flask with the bottom covered 1 cm. deep with small gypsum plates was brought about 1 liter of conductivity water, all at the temperature of the bath, and the liquid rotated about fifty times per minute, and since the gypsum plates were not disturbed the solution above was always

clear. From this every five or ten minutes (at first), 10 cm^3 was removed and its conductivity determined. Under these conditions, which could not be regarded as overfavorable for rapid saturation, it was found that saturation took place in from forty to ninety minutes, depending on the temperature, as can be seen in column VII. Of course the rate of solution depends on several factors, but in the case of gypsum it seems to be fairly rapid, and this agrees with the observations of Bruner and Tallocyko.[1]



○ "Dwey's results" in diagram should read "Droez's results."

Cameron[2] assumes that the rate of solution is very slow and endeavors to explain the discrepancies in the published solubility results as due to undersaturated solutions, whereas the results generally are on the other side of normally saturated solutions.

The preceding table gives the results of normally saturated solutions starting from water and gypsum and assuming that equilibrium was reached when the conductivity of the liquid was

[1] *Ztschr. anorg. Chem.*, 28, 320.
[2] *J. Phys. Chem.*, 8, 567.

constant, although in all cases the liquid was rotated over the gypsum plates for an extra hour or two before the analysis was made. A solution saturated at 25° C. (or which from conductivity showed 15.29 milligram-molecules per liter) was brought to 0° and rotated in contact with the gypsum plates. The conductivity slowly decreased but it required two days, or forty-eight hours to become constant, and analysis gave for 100 cm^3 0.1758 gram calcium sulphate, whereas the solution starting from water and gypsum at 0° C. gave 0.1760 and 0.1758 gram while the conductivity of the two solutions was the same.

At 25° C. the system water-gypsum showed a constant conductivity of 0.002206 in seventy-five minutes, while the previous work[1] showed that a solution saturated at 35° C. and brought to 25° C. gradually decreased in conductivity, and after twelve hours reached the normal value $\lambda = 0.002208$. These results show that our method gave us equilibrium, but it was deemed advisable to test this point above the change in the solubility curve at 40° C., so 50° C. was the temperature selected; first a saturation was made at 38° C.; then the system was brought to 50° C., where it was found that the solubility slowly decreased and next morning had already become constant. An analysis of the solution gave per 100 cm^3 0.2049 gram and 0.2045 gram calcium sulphate respectively. Water and gypsum plates were brought together at 50° C., and in about forty minutes the conductivity had become constant, and an analysis showed 0.2040 gram calcium sulphate in 100 cm^3. In these experiments evaporation from the solution was prevented in the same manner as in the experiment at 100° C.

These experiments seem to settle conclusively the question of equilibrium. Above 50° the conductivity seems to indicate that the glass of the flask was slightly attacked, although not enough to sensibly affect the solubility results.

The early works on the solubility of gypsum have only a historical interest, although the result given by Giese[2] of 380 parts of cold water to dissolve 1 gram of gypsum is not far wrong for room temperature; but 388 parts of boiling water to 1 of gypsum is quite wrong. Tipp[3] also gives 388 parts of water to 1 of gypsum at 15°-20° C.

[1] *Ztschr. phys. Chem.*, 37, 391.
[2] Auflage Gmelin's Handbuch, Vol. V., 183.
[3] *Jahresbericht*, (1864), 8, 325.

Marignac[1] showed that it was exceedingly easy to obtain a supersaturated solution of gypsum and that such a solution was very slow to come to equilibrium, even in the presence of an excess of the solid gypsum. Marignac made determinations between 0° and 100°, taking care to have an excess of finely divided gypsum uniformly distributed through the solution, and the system was undoubtedly in equilibrium before a part of the clear solution was analyzed. He was able to show that the results of his predecessors were affected by the phenomena of supersaturation.

Droez[2] confirmed Marignac's results and added several of his own. He especially showed that the equilibrium could be reached from either side, emphasizing the necessity of an excess of the finely divided gypsum and constant agitation. Droez also took account of the density of water in his calculations. He assumed the density of his solution to be the same as that of water at the same temperature, and gave a table of solubilities from 0° to 100° C. from a curve of his and Marignac's results. Both of these workers avoided supersaturation in the sense that their solutions were in equilibrium with the solid present. Still, from the method of these experiments and the results, the solid must have

TABLE II.

	I.	II.	III.	IV.
T°.	Poggiale.	Marignac.	Droez.	Normally saturated solutions.
0	15.06	14.00	...	12.91
5.5	...	...	14.11	13.56
14.2	...	...	14.83	14.50
18	...	15.06	...	14.81
19.5	...	...	15.66	14.88
20	17.72	...	...	14.95
24	...	15.30	15.87	15.23
32	...	15.64	...	15.38
35	18.75	...	...	15.40
36	...	...	16.19	15.41
38	...	15.79	..	115.41
41	...	15.71	...	15.39
53	...	15.52	...	14.85
72	...	14.86	...	12.70
86	...	13.94	...	12.70
99	...	12.89	...	11.95
100	...	...	...	11.90

[1] *Ann. chim. phys.*, (5) 1, 274 (1874).
[2] *Ber. d. chem. Ges.*, (1877), p. 330.

been very finely divided, that is, having some particles less than 2 microns in diameter since their solutions were about 5 per cent. more concentrated than normally saturated solutions. The results of these two workers have been accepted as the most reliable, so they have been calculated to millimolecules per liter and given in Table II (preceding page), together with the concentrations of normally saturated solutions taken from the curve of our results.

Kohlrausch and Rose[1] give results of conductivity of solutions saturated at various temperatures. A comparison of these data with the conductivity of known solutions[2] shows that their solutions were some 4 per cent. too concentrated. There are a great many determinations of the solubility of gypsum or crystallized $CaSO_4.2H_2O$ by various workers, and even where care was taken to avoid supersaturation, the results generally distinctly show the influence of surface-tension. There are two exceptions, Cossa and Church, who made determinations at about 20° and 13°; their results are 10.5 per cent. and 12 per cent. respectively *below* the normally saturated solutions. We have not been able to consult the original publications so we cannot judge of the material or the method used. The previous work[3] showed that in the case of gypsum the surface-tension plays a decided rôle in the solubility, for it was found possible to increase the solubility (at 25°) 20 per cent. by grinding the gypsum powder in an agate mortar, but the system so obtained was not in final equilibrium, since the smaller particles grew smaller and disappeared while the larger ones grew in size. This is, however, a slow process[4] with gypsum and does not reach final equilibrium (the normally saturated solution) in five days, while if the stirring is too rapid, the abrasion from the soft gypsum continually yields a fine powder, and a normally saturated solution is never attained. Plates of gypsum rotated with water in a flask, as is ordinarily done in solubility determinations, will easily yield a 5 per cent. too great solubility. On the other hand the results here obtained show that slowly rotating a liquid over the plates will give a saturated solution in about an hour's time. These facts give a satisfactory explanation of the irregularities in the published determinations.

[1] *Ztschr. phys. Chem.*, 12.
[2] *Ibid.*, 37, 371.
[3] *Ibid.*, 37, 392.
[4] *Loc. cit.*, p. 394.

The solubility curve of gypsum is of special interest on account of the change in the direction of the curve. This fact was discovered by the early workers, and from Marignac's and Droez's results the maximum solubility is given at 38° C. while the curve of the results here obtained indicates 40° C. as the temperature at which there is the greatest concentration. From here the concentration decreases with the temperature and at 90° is the same as at 0°, while at 107° it has decreased some 12 per cent. further. There seems to be no break in the curve at 40° as we had expected to find, while the vapor-pressure curve of water compared to that of gypsum, plotted from the interesting results of van't Hoff and Armstrong,[1] show a perfectly uniformly increasing difference from 0° to 85°, where the vapor-pressure of water is some 85 mm. greater than that of gypsum. At 40° the difference is 29 mm. From 85° on the difference decreases, and at 107° the lines cross and the half hydrate appears (a saturated solution of gypsum must have a vapor-pressure that is only a few hundredths of a millimeter less than that of pure water). The uniformity of the vapor-pressure curve of gypsum excludes the idea of explaining the change at 40° (from increasing to decreasing solubility) by assuming the appearance of a new phase. Thermodynamics connects this change at 40° with the change of the sign of the heat of solution. This question has been thoroughly discussed by van't Hoff[2] where the case of gypsum is considered. It is to be noted that this is a thermodynamic relation and while it is experimentally supported by the observations of Berthelot on the heat of precipitation of $CaSO_4.2H_2O$ above and below 40°, we are still in the dark as to why the curve takes a downward curve at 40°.

In the case of slightly soluble substances the effect of the dissolved substance on the solvent can be neglected, while in the case of more soluble substances the nearly saturated solution is a quite different agent from the pure solvent,[3] so it seems probable that general relations will first be found in connection with less soluble substances and the results of this paper indicate that there is need of a careful redetermination of such data with due regard to the influence of surface-tension.

DEPARTMENT OF GENERAL CHEMISTRY,
UNIVERSITY OF MICHIGAN,
March, 1902.

[1] *Sitz. Ber.* (1900), p. 559.

[2] Vorlesungen, p. 31.

[3] Nernst: "Theoretische Chemie," p. 445.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(FOURTH PAPER.)

BY HENRY L. WHEELER AND TREAT B. JOHNSON.

Received April 11, 1902.

THE work described in this paper was undertaken with the object of investigating the behavior of some tertiary halides towards alcoholic solutions of potassium thiocyanate. Up to the present time no tertiary alkyl halide has been found to give an isothiocyanate or mustard oil. This property has only been observed in the case of the primary allyl halides and the secondary diphenylmethyl bromide. In fact this subject has hitherto received little attention. Of the three tertiary halides that have been examined triphenylmethyl bromide and α-bromisobutyric ethyl ester gave normal thiocyanates while tricarbethoxymethane failed to react.[1]

The tertiary halides which we now discuss comprise all the possible compounds formed by substituting the positive group methyl, and the negative radicals, phenyl and carbethoxyl, $-CO.OC_2H_5$, for hydrogen in methyl bromide.[2] There are ten combinations to be considered; and among these, it will be noticed, are the above three tertiary forms that have already been examined:

I. $BrC(CH_3)_3$	VI. $BrCCH_3(CO_2C_2H_5)_2$
II. $BrC(CH_3)_2C_6H_5$	VII. $BrC.CH_3.C_6H_5.CO_2CH_3$
III. $BrCCH_3(C_6H_5)_2$	VIII. $BrC(CO_2C_2H_5)_3$
IV. $BrC(C_6H_5)_3$	IX. $BrCC_6H_5(CO_2C_2H_5)_2$
V. $BrC(CH_3)_2CO_2C_2H_5$	X. $ClC(C_6H_5)_2CO_2C_2H_5$

The investigation has shown that six of these compounds give normal thiocyanates, while the remaining four give neither normal or isothiocyanates.

Tertiary butyl bromide (I) reacted smoothly with alcoholic

[1] Since the above was written Crocker has found that picryl chloride gives an isothiocyanate. *Jour. Chem. Soc.* (London), 81, 436 (1902).

[2] In one case (VII) the methyl ester was used and in another (X) the chloride instead of the bromide was employed; experience has shown that the bromides react more readily than the chlorides.

potassium thiocyanate, and the product was shown to be a normal thiocyanate by combining it with thioacetic acid, whereupon acetyl dithioisobutyl urethane, $CH_3CONHCSSC_4H_9$, was obtained

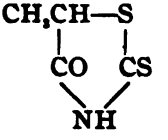
1'-Bromisopropyl benzene (II), 1'-brom-1,1-diphenylethane, (III), 1'-bromhydratropicmethyl ester (VII), and tricarbethoxymethyl bromide (VIII) reacted readily with, or were decomposed by, potassium thiocyanate, and a bright yellow, amorphous precipitate separated which had the properties of the so-called pseudocyanogen sulphide. These bromides therefore act like free bromine on potassium thiocyanate. The behavior of tricarbethoxymethyl bromide, in reacting immediately in the cold, is in strong contrast to that of the chloride, which showed little tendency to react even on heating for a number of hours.

Triphenylmethyl bromide (IV), as previously stated, gave a normal thiocyanate. In this case the rhodanide formed thiol esters with thioacetic and thiobenzoic acids.

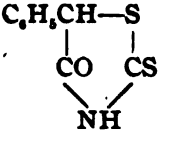
α-Bromisobutyric ethyl ester (V) also gave a normal thiocyanate. This was shown by boiling the product with hydrochloric acid, whereupon α-μ-diketo-β-dimethyltetrahydrothiazole, was obtained.

Methylbrommalonic ester (VI) readily reacted with potassium thiocyanate, while ethyl chlormalonic ester remained unaltered even when heated with potassium thiocyanate to 140°-145° for a number of hours. When the product, in the case of methylbrommalonic ester was warmed with thioacetic acid, a thick oil was obtained which, on dissolving in alkali and precipitating with hydrochloric acid, gave α-keto-μ sulpho-β-methylthiazolidine, the so-called α-rhodaninpropionic acid.[2] The structure of this is represented by formula XI. That the rhodanide is a normal thiocyanate is shown by the fact that the reaction took place as follows:

$$CH_3CONHCSSCCH_3(CO_2C_2H_5)_2 + NaOH + H_2O =$$
$$C_4H_5ONS_2 + CH_3COONa + CO_2 + 2C_2H_5OH.$$



XI.



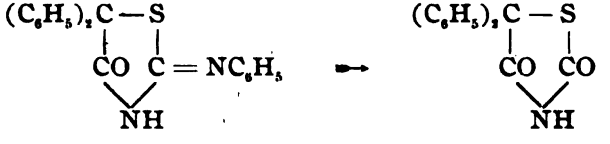
XII.

[1] *Am. Chem. J.*, 24, 78 (1900).

[2] Berlinerblau: *Ber. d. chem. Ges.*, 19, 125.

Bromphenylmalonic ester (IX) reacted smoothly with potassium thiocyanate, and the product with thioacetic acid and alkali behaved in a similar manner, inasmuch as α-keto-μ-sulpho-β-phenylthiazolidine (XII) was obtained.

Diphenylchlorethyl acetate (X) gave the first and only rhodanide that has failed to react with thio acids. It reacted, however, with aniline, yielding triphenylpseudothiohydantoïn (XIII). On warming the latter with alcoholic hydrochloric acid, α-μ-diketo-β-diphenyl tetrahydrothiazole was obtained (XIV).

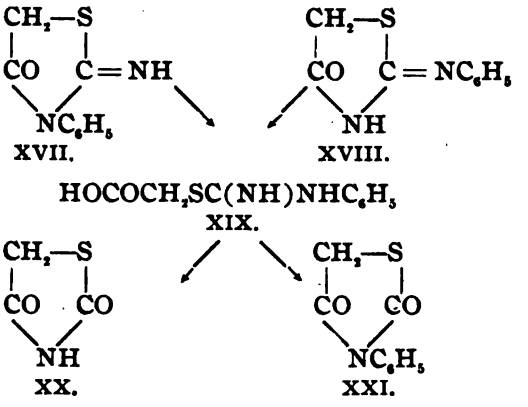


XIII. XIV.

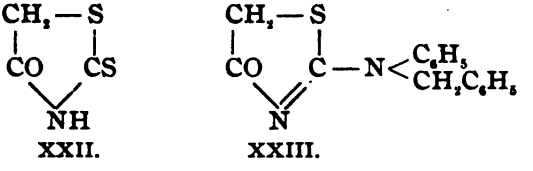
The behavior of this hydantoïn with hydrochloric acid differs from that of the pseudothiohydantoïn from phenylthiocyanethyl acetate,[1] inasmuch as the latter, under certain conditions, gives up ammonia and not aniline on boiling with hydrochloric acid; generally, however, a mixture is obtained. The behavior of phenylpseudothiohydantoïn with hydrochloric acid has been supposed to show that the compound has the structure represented by formula XVII.

We have found that this long-known phenylpseudothiohydantoïn which, according to Meyer,[2] Liebermann,[3] and Dixon,[4] gives α,μ-diketo-N-phenyltetrahydrothioazole ("phenylsenfoelglycolid"), formula XXI, with hydrochloric acid, also gives α,μ-diketotetrahydrothiazole (XX). It follows from this that the reaction with hydrochloric acid can not be used to decide the structure of these thiohydantoïns. Both of the theoretically possible isomeric phenylpseudothiohydantoïns, (XVII) and (XVIII), for example, can give phenylthiohydantoic acid (XIX), and this can be decomposed into the two tetrahydrothiazoles that are actually obtained:

[1] *Am. Chem. J.*, **26**, 353 (1901).
[2] *Ber. d. chem. Ges.*, **14**, 1661 (1881).
[3] *Ann. Chem.* (Liebig), **207**, 129 (1881).
[4] *J. Chem. Soc.* (London), **71**, 620 (1897).



Dixon found that the hydantoïn in question gave α-keto-μ-sulphotetrahydrothiazole ("rhodanininsäure"), formula, XXII below, when heated with carbon disulphide, and he therefore assigned to the compound the structure represented above by formula XVIII. This is undoubtedly correct since by the action of benzyl chloride and alkali, a benzyl derivative is obtained from this hydantoïn, which is identical with that from benzylphenylthiourea, $C_6H_5(C_6H_5CH_2)NCSNH_2$, ethylchloracetate and alkali. This benzyl derivative must have the structure represented by formula XXIII:



EXPERIMENTAL PART.

I.—*Tertiary Butyl Bromide* $(CH_3)_3CBr$, *and Potassium Thiocyanate.*—The bromide was made by the union of isobutylene and hydrogen bromide. The purified material reacted immediately when warmed with an alcoholic solution of potassium thiocyanate, and potassium bromide separated. The product was an oil which possessed a strong, pungent odor. It could not be distilled under reduced pressure without decomposition and therefore, for analysis, it was simply washed and dried in a desiccator over sul-

phuric acid. A nitrogen determination then gave:

	Calculated for C_9H_9NS.	Found.
Nitrogen	12.17	12.48

Tertiary Butyl Rhodanide and Thioacetic Acid.—Eight grams of the rhodanide and 6 grams of thioacetic acid were heated on the water-bath in benzene for eight hours. On cooling, a white flocculent precipitate separated. This crystallized from benzene in scales or plates, and did not melt at 260°. It was extremely soluble in alcohol, contained nitrogen but no sulphur, and was soluble in a solution of sodium hydroxide. A sufficient amount of this was not obtained for identification. Two determinations gave 10.88 and 11.01 per cent. nitrogen. The oil that remained, after evaporating the benzene, solidified on cooling; it was dissolved in dilute sodium hydroxide and the solution shaken with ether. From the alkaline solution acetic acid precipitated a bright yellow body which, on crystallizing from petroleum ether, melted at 112°-113°. Its solubility in sodium hydroxide, its yellow color and the following nitrogen determination show that this material is *tertiary butylacetyldithiocarbamate,* $CH_3CONHCS.SC(CH_3)_3$.

	Calculated for $C_7H_{13}ONS_2$.	Found.
Nitrogen	7.33	7.32

II.—*1'-Bromisopropyl Benzene, $C_6H_5CBr(CH_3)_2$, and Potassium Thiocyanate.*—Isopropyl benzene was prepared from normal propyl chloride and benzene by means of the Friedel-Crafts reaction. The material used boiled at 152°-154° at ordinary pressure. Eight grams of the hydrocarbon were brominated at 115°-120° with the calculated quantity of bromine. The product was washed thoroughly with a solution of sodium carbonate, extracted with ether, and dried in a vacuum. It was impossible to purify this new bromide by distilling under diminished pressure since an attempt at 16 mm. resulted in rapid decomposition taking place at about 135°, with evolution of hydrogen bromide. A bromine determination agreed with the calculated, probably as closely as could be expected.

	Calculated for $C_9H_{11}Br$.	Found.
Bromine	40.20	38.10

This bromide immediately reacted with potassium thiocyanate in warm alcohol, and a fine yellow powder separated. The latter

possessed all the properties of *pseudocyanogen sulphide.* The material remaining in the alcoholic solution proved to be an oil but not enough of this was obtained to establish any definite boiling-point.

III.—*1',1'-Diphenyl-1'-Bromethane,* $(C_6H_5)_2CBrCH_3$, *and Potassium Thiocyanate.*—Diphenylethane was prepared from ethylidine chloride (from paraldehyde and phosphorus pentachloride) and benzene by means of the Friedel and Crafts reaction. It was found that this hydrocarbon could not be brominated in the usual manner for the preparation of other halogen derivatives of benzene in the side-chain, owing to the ease with which the bromide loses hydrogen bromide. After several unsuccessful attempts it was found that a product consisting essentially of the desired bromide could be prepared by brominating the hydrocarbon at 100°-105°. The product, washed with sodium carbonate and water and dried in a vacuum desiccator, gave the following result on analysis:

	Calculated for $C_{14}H_{13}Br$.	Found.
Bromine	30.6	24.37

When a product thus prepared was distilled at 10 mm. pressure, it rapidly decomposed with evolution of hydrogen bromide. On continuing the distillation, it practically all boiled at 155°-165°. Diphenylethylene boils at 162° at 15 mm. pressure, according to Anschütz.[1] The crude bromide reacted at once with potassium thiocyanate in alcohol, *pseudocyanogen sulphide* separated, and an oil was obtained that boiled at 150°-162° at 11 mm. pressure. (Diphenylethylene?)

IV.—*The Action of Triphenylmethyl Bromide on Potassium Thiocyanate,* which resulted in the formation of a normal thiocyanate, was described in our second paper.[2]

V.—*Ethyl-α-Bromisobutyric Ester Gave Ethylnormalthiocyanisobutyrate,*[3] as shown in this laboratory by Mr. Le B. Gray. The thiocyanate reacts normally with thiobenzoic acid, and *benzoyldithioethyl-α-isobutyrate carbonate,*

$$C_6H_5CONHCS.SC(CH_3)_2CO_2C_2H_5,$$

is formed. This separates from a mixture of benzene and petro-

[1] *Ann. Chem.* (Liebig), 235, 159.
[2] *Loc. cit.*
[3] *Loc. cit.*

leum ether in the form of yellow prisms, which melt at 113°-114°. It is extremely soluble in alcohol.

	Calculated for $C_{14}H_{17}O_2NS_2$.	Found.
Nitrogen	4.50	4.37

VI.—*Brommethylmalonic Ethyl Ester, $CH_2CBr(CO_2C_2H_5)_2$, and Potassium Thiocyanate.*—Methylmalonic ester was brominated at 65°; the product practically all boiled at 112°-118° at 14 mm. pressure. A bromine determination in a portion of this boiling at 114° gave 31.6 per cent. while the calculated is 31.62 per cent. bromine.

When this bromide was mixed in alcohol with potassium thiocyanate it immediately began to react. The mixture was warmed for about a half hour, on the steam-bath, and then water precipitated an oil possessing a strong penetrating odor. It all boiled at 139°-142° at 9 mm. pressure; a portion boiling at 140° was analyzed with the following result:

	Calculated for $C_9H_{13}O_4NS$.	Found.
Nitrogen	6.06	6.15

Five grams of this rhodanide, 2 grams of thioacetic acid and 10 cc. of benzene were heated on the water-bath for twelve hours. After evaporating the benzene, an oil was obtained which would not solidify in a freezing-mixture. The oil dissolved in a dilute solution of sodium hydroxide and was not precipitated with carbon dioxide; dilute acetic acid, on the other hand, precipitated a yellow solid which was purified by crystallizing from alcohol and benzene. It then formed plates which melted at 124° and showed no effervescence when heated to 175°. Nitrogen determinations agreed with the calculated for *α-keto-μ-sulpho-β-methylthiazolidine:*

	Calculated for $C_4H_5ONS_2$.	Found. I.	Found. II.
Nitrogen	9.52	9.28	9.58

In fact this compound is identical with the so-called "α-rhodaninpropionsäure" of Berlinerblau[1] which was obtained from chlorpropionic acid and ammonium thiocyanate. Berlinerblau gives the melting-point at 123°.

VII.—*α-Bromhydratropicmethyl Ester, $CH_3CBr(C_6H_5)CO_2CH_3$, and Potassium Thiocyanate.*—Although the preparation of hydra-

[1] *Ber. d. chem. Ges.*, 19, 125.

tropicmethyl ester, by the method which we adopted, includes ten stages, nevertheless the brom-derivative can be more easily obtained, in quantity, by the following procedure than by the method which involves the preparation of atrolactinic acid. On the other hand, a purer product is undoubtedly obtained by the action of hydrogen bromide on atrolactinic acid.[1]

Starting with benzyl chloride we prepared the cyanide, phenylacetic acid, the ethyl ester, and from the latter phenyloxalacetic-ethyl ester[2] which gave phenylmalonic ester. Eighty grams of this were prepared boiling at 159.5°-160° at 12 mm. pressure. This was methylated[3] and 60 grams of phenylmethylmalonic ester resulted, which boiled at 12 mm. pressure at precisely the same point as the unaltered material. On saponifying this, 21 grams of methylphenylmalonic acid were obtained, melting at 155°-156°. When this was heated and the resulting hydratropic acid was esterified, 13 grams of methyl ester were obtained, which boiled at 218°-221° at ordinary pressure Neure[4] gives the boiling-point of this ester at 221°. The bromination of this was conducted in an oil-bath at 150°. The dark-colored product was washed with water and sodium carbonate and an attempt was made to purify a portion by distilling under diminished pressure, whereupon it was found that the oil underwent decomposition, giving off hydrogen bromide. The washed product was therefore warmed directly with an alcoholic solution of potassium thiocyanate (through an oversight no portion of the oil was reserved for analysis). The products of the reaction consisted of *pseudocyanogen sulphide* and an oil. The latter, since it was not a rhodanide, was not examined.

VIII.—*Tricarbethoxymethyl Bromide, $C.Br(CO_2C_2H_5)_3$, and Potassium Thiocyanate.*—Tricarbethoxymethane was easily brominated on the water-bath and the product boiled, for the most part, at 162°-163° at 16 mm. pressure. The colorless oil thus obtained was analyzed with the following result.

	Calculated for $C_{10}H_{15}O_6Br$.	Found.
Bromine.....	25.7	25.5

When this bromide was warmed in alcohol with potassium thio-

[1] Fittig and East: *Ann. Chem.* (Liebig), **206**, 28 (1881).
[2] Wislicenus: *Ber. d. chem. Ges.*, **27**, 1093.
[3] Wislicenus and Goldstein: *Ibid.*, **28**, 815.
[4] *Ann. Chem.* (Liebig), **230**, 152.

cyanate, it reacted at once and *pseudocyanogen sulphide* separated. On adding water to the alcoholic solution an oil was obtained. This was distilled at 10 mm. pressure and although there was no apparent decompositon, during the distillation, it started to boil at about 141° and continued up to 177°. The bromide therefore reacts with potassium thiocyanate with decomposition.

IX.—*Phenylbrommalonicethyl Ester,* $C_6H_5C.Br(CO_2C_2H_5)_2$, *and Potassium Thiocyanate.*—This bromide was obtained by brominating phenylmalonicethyl ester at 140°-150°. It formed a colorless oil which was found to boil at 192° at 20 mm. pressure and, from another preparation, at 177°-181° at 11 mm. pressure. A bromine determination in the first case gave:

	Calculated for $C_{13}H_{15}O_4Br$.	Found.
Bromine	25.38	24.98

When this bromide was treated with potassium thiocyanate an oil was obtained which could not be purified by distilling under diminished pressure. At 20 mm. rapid decomposition took place at about 200°. The oil, after washing with water and drying, was analyzed with the following result:

	Calculated for $C_{14}H_{15}O_4NS$.	Found.
Nitrogen	4.77	5.37

The nitrogen determination agrees, perhaps as well as could be expected, for a non-rectified oil, with the calculated for *thiocyanphenylmalonicethyl ester,* $C_6H_5C(SCN)(CO_2C_2H_5)_2$.

Ten grams of this rhodanide and 3 grams of thioacetic acid were heated in benzene for twenty-four hours, whereupon, on evaporating the benzene, an oil was obtained which refused to solidify. It was dissolved in cold dilute sodium hydrate and, after standing, was precipitated with dilute hydrochloric acid. This treatment gave a yellow solid, which, on crystallizing from alcohol, formed yellow prisms and melted at 178°-179° without effervescence. A nitrogen determination agreed with the calculated for *α-keto-μ-sulpho-β-phenylthiazolidine:*

	Calculated for $C_9H_7ONS_2$.	Found.
Nitrogen	6.69	6.51

Thiocyanmethylmalonic ester and thiocyanphenylmalonic ester therefore behave in an analogous manner with thioacetic acid and

alkali. The reaction proves that these rhodanides are normal thiocyanates.

X.—*Diphenylchloraceticethyl Ester,* $(C_6H_5)_2C.Cl.CO_2C_2H_5$, *and Potassium Thiocyanate.*—The chlorester was made by treating benzilic acid with phosphorus pentachloride and then pouring the acid chloride into cold alcohol.[1]

When this chloride was warmed in alcoholic solution with potassium thiocyanate for about five hours the reaction was complete. On evaporating, an oil was obtained which had a most remarkable behavior on heating. On attempting to distil under reduced pressure no signs of decomposition could be observed, but no matter at what rate the distillation was conducted it frothed over in one continuous stream, and no fractionation could be accomplished. A nitrogen determination was therefore made in a sample of crude product that was washed and dried over sulphuric acid.

	Calculated for $C_{17}H_{15}O_2NS$.	Found.
Nitrogen.....	4.7	4.2

This rhodanide is distinguished from all others that have been examined by the fact that it does not react with thioacetic or thiobenzoic acids, on warming in benzene for the usual length of time (two to twenty-four hours).

The oil, recovered from the treatment with thiobenzoic acid, was heated with aniline on the steam-bath for from five to six hours. On washing the product with dil te hydrochloric acid and crystallizing from alcohol, colorless prisms were obtained which melted at 250°. This, on analysis, gave the following result which agrees with the calculated for *triphenylpseudothiohydantoin.*

	Calculated for $C_{21}H_{16}ON_2S$.	Found.
Nitrogen.....	8.13	8.14

When this substance was dissolved in alcohol and warmed for a short time with concentrated hydrochloric acid, a product was obtained which crystallized from dilute alcohol in colorless prisms and melted at 144°-145°. An examination of the acid solution showed that aniline had been removed by this treatment and the

[1] Bickel: *Ber. d. chem. Ges.*, 22, 1537.

crystalline material gave results agreeing with the calculated for *α-μ-diketo-β-diphenyltetrahydrothiazole:*

	Calculated for $C_{15}H_{11}O_2NS$.	Found.
Nitrogen	5.20	5.24

In our second paper on thiocyanates it was shown that ethyl phenylthiocyanacetate reacts with aniline, giving a compound that was considered to be diphenylpseudothiohydantoïn. We now find that ethylphenylchloracetate and phenylthiourea give the same compounds. This proves that these compounds are pseudothiohydantoïns. On boiling the compound from phenylthiourea with 30 per cent. hydrochloric acid a compound was obtained that crystallized from alcohol in needles and melted at 173°-174°. A nitrogen determination agreed with the calculated for *α-μ-diketo-β-phenyl-*N*-phenyltetrahydrothioazole:*

	Calculated for $C_{15}H_{11}O_2NS$.	Found.
Nitrogen	5.20	5.44

Benzylphenylpseudothiohydantoïn.—This was obtained by warming 5.5 grams of phenylpseudothiohydantoïn, 6.5 grams of sodium dissolved in 55 cc. of alcohol and 20 cc. of water, and 3.6 grams of benzyl chloride, until the mixture no longer gave an alkaline reaction. When the alcohol was evaporated, the residue taken up in ether and shaken with alkali, and the product crystallized from alcohol, beautiful, colorless, transparent, square tables were obtained which melted at 124°-125°.

The same compound was obtained by warming 4 grams of unsymmetrical benzylphenylthiourea and 3 grams of ethyl chloracetate, in alcoholic solution, for a number of hours. The alcohol was then evaporated and the residue treated with alkali. On crystallizing from alcohol, square tables melting at 124°-125° resulted and when mixed with the above preparation the melting-point was not altered.

Dixon prepared this benzylphenylpseudothiohydantoïn, by a different method. He states that it melts at 118°-119° (corr.).

NEW HAVEN, CONN.,
April 8, 1902.

NOTES.

Notes upon the Constants of Some Little Known Oils.—

Specific gravity at 22°.

Oil of nigella	0.9093
Oil of boldo leaves	0.9189
Oil of matico	1.1205
Oil of cascarilla	0.9116
Oil of milfoil	0.9217
Oil of wildmint	0.9942 at 20°.

Refractive index at 24° (sodium flame).

Oil of nigella	1.494
Oil of boldo leaves	1.471
Oil of matico	1.513
Oil of cascarilla	1.485
Oil of galanga	1.472
Oil of wildmint	1.487
Oil of milfoil	1.486

Taken with a Bertrand refractometer.

Solubility of the Oils in 80 Per Cent. Alcohol at 22°.

Oil of nigella not perfectly clear in 23 parts of alcohol by volume.

Oil of boldo leaves soluble in 1 or even less volumes.

Oil of matico soluble in 3½ to 4 parts by volume.

Oil of cascarilla, solution not perfect in 20 volumes.

Oil of wildmint soluble in about 1½ volumes.

The oil of wildmint rotates the plane of polarized light to the right 12.59° at 21.7°.

The quantity of these oils was very slight so that no chemical examination could be made. They were distilled by Schimmel & Co., and obtained from Fritsche Brothers, their representatives in the United States.

A. B. AUBERT.

UNIVERSITY OF MAINE,
ORONO, MAINE.

NEW BOOKS.

WATER SUPPLY (Considered principally from a sanitary standpoint). By WILLIAM P. MASON. Third edition. Rewritten. 448 pp. New York: John Wiley & Sons. Cloth. Price, $4.00.

The first edition of this extremely useful book appeared in 1896 and was noticed at length in this Journal. The chapters relating

to methods of chemical and bacterial examination of water which were a part of the earlier edition are now omitted, as they have since been expanded and published as a separate work. Much new matter has been added, however, to this third edition, and all important recent discussions seem to have received attention. At the present time few topics are of greater public interest than are those connected with questions of water purification on the large scale. The chapter dealing with this subject is full of timely information and is quite sufficient to give the general scientific reader a good idea of various practical methods and appliances.

J. H. LONG.

NOTES ON LEAD ORES. BY JAMES FAIRIE, F.G.S. London: Scott, Greenwood & Co. 62 pp. 16mo. Price, $1.00.

The book consists of a collection of information concerning all the lead minerals, including occurrence, hardness, specific gravity, blowpipe tests, and composition—just what is to be found in any standard work on mineralogy. It is well printed in large type.

E. H. M.

GAS AND FUEL ANALYSIS FOR ENGINEERS. A compend for those interested in the economical applications of fuel. BY AUGUSTUS H. GILL, S.B., Ph.D. Third edition. New York: John Wiley & Sons. 1902. iv + 104 pp. Price, $1.25.

According to the preface the substance of this book was given in the form of lectures to students in the courses of chemical, mechanical and electrical engineering at the Massachusetts Institute of Technology, Boston.

The author discusses in an exceedingly brief and yet clear and satisfactory manner the common forms of apparatus for technical gas analysis, their manipulation and uses. The methods of taking gas samples, their analysis, the measurement of the temperature of chimney gases, the preparation of reagents, the arrangement of the gas laboratory, and the calorimetric determination of fuel values are treated in separate chapters. Useful calculations in relation to the combustion of fuels together with some valuable tables add to the merits of the book. The illustrations serve fully for the elucidation of the text. The treatment of the subject is excellent and the book can be recommended as a useful aid to students of gas analysis.

F. C. P.

THE AMERICAN YEARBOOK OF MEDICINE AND SURGERY FOR 1902. VOL. I, GENERAL MEDICINE. Philadelphia: W. B. Saunders & Co. 1902. 700 pp. Cloth, $3.00 net. Half morocco, $3.75 net.

This excellent work, which has been issued for a number of years, is under the editorial charge of George M. Gould, M.D., and presents brief summaries of the most important contributions to medical literature made during the preceding year. While naturally intended for practitioners of medicine the book will be found valuable and interesting by those chemists who desire to keep in view the advances in a field closely related to their own in many points. The fundamental importance of chemistry in medicine is becoming more clearly recognized from year to year, and this is well shown by a perusal of the pages of the Yearbook.

J. H. LONG.

INDICATORS AND TEST-PAPERS: Their Source, Preparation, Application, and Tests for Sensitiveness. A Résumé of the Current Facts Regarding the Action and Application of Indicators and Test-Papers Which Have Been Proposed from Time to Time, and are in Present Use in Chemical Manipulation, with a Tabular Summary of the Application of Indicators, Designed for the Use of Chemists, Pharmacists, and Students. BY ALFRED I. COHN, PH.G. Second Edition, Revised and Enlarged. First thousand, New York: John Wiley & Sons; London: Chapman & Hall, Limited, 1902. pp. ix + 267. Price, $2.00.

The first edition of this work which was reviewed in this Journal, 1899, p. 1176, now appears with an appendix containing the description of ten additional indicators in the style of the previous work. The book is a useful addition to the practical chemist's list of dictionaries. References to original articles are unfortunately not given.

The present writer agrees perfectly with the former reviewer in believing that Mohr's unsupported assumption of the cause of color had better have been omitted, and that the isolated discussion of the theory of indicators could well have been improved in the new edition.

W. R. WHITNEY.

A TEXT-BOOK OF INORGANIC CHEMISTRY. BY DR. A. F. HOLLEMAN, rendered into English by HERMON C. COOPER, PH.D. John Wiley & Sons. 1902. viii + 458 pp. Price, $2.50.

The difficult task of incorporating the ideas of the newer physical chemistry with the general descriptive matter necessary in a

text intended to introduce the student to chemical studies has been undertaken by the author of this work with boldness and discretion. The theory is not separated from the facts to which it belongs, but it is in every instance treated as an intimate part of them.

The concept of atoms and molecules is developed at an early stage, after a brief treatment of the properties and composition of water. The kinetic theory, dissociation, law of mass action, methods of determining molecular weights and several related topics are discussed, hand in hand with the description of the elements of the halogen group, and are treated with admirable precision and clearness. The question forces itself, however, upon the reader, whether it is wise to compress so large a part of the theory into the first eighty pages.

The presentation of the principles of thermochemistry is very satisfactory and that of the periodic system is adequate, the customary atomic volume curve being reproduced according to recent data.

A good deal of space is devoted to technological processes, eight pages being given, for example, to the manufacture of sulphuric acid. The few words relating to spectrum analysis could scarcely be improved upon.

The book as a whole has a marked air of scholarly distinction, for which part of the credit belongs to the translator. Very few passages bear any of the ear-marks of translation which too often disfigure American editions of foreign scientific books. While the descriptive matter is subordinated to the consideration of principles, it does not seem to the reviewer that the author has gone too far in this direction. It would not be impossible for some college classes to cover the entire ground of the text in a year's work. LAUNCELOT W. ANDREWS.

A BIBLIOGRAPHY OF THE ANALYTICAL CHEMISTRY OF MANGANESE, 1785–1900. BY HENRY P. TALBOT AND JOHN W. BROWN. City of Washington: Published by the Smithsonian Institution. 1902. pp. viii+124.

This is the fourteenth of the bibliographies pertaining to chemical subjects published by the Smithsonian Institution on recommendation of a Committee of the American Association for the Advancement of Science of which Dr. H. C. Bolton is Chair-

man. For the portion 1785 to 1830 the present Bibliography is based largely on "An Index to the Literature of Manganese, 1596-1874," published by Dr. Bolton in 1875. The present work is, however, confined to the analytical part of the subject and is, apparently, very complete for that field. W. A. N.

JAHRBUCH DES VEREINS DES SPIRITUS-FABRIKANTEN IN DEUTSCHLAND, DES VEREINS DER STÄRKE-INTERESSENTEN IN DEUTSCHLAND UND DER BRENNEREI-BERUFSGENOSSENSCHAFT. Zweiter Jahrgang, 1902. 8vo. xvi + 471 pp. Berlin: Paul Parey. 1902.

This second volume of the Jahrbuch is edited by Dr. Delbruck and its high value to the fermentation and cereal products industries is thereby assured. And this volume certainly establishes the success of the undertaking to publish it.

The editor states in the preface that "the compass of the work has considerably extended this year, not because of prolixity on the part of reporters but because of the enormous increase in material to be treated, and in his oral report to the societies in their general meeting he says "the object of the yearbook is that the members may have the work of the year not in the detached parts of our Journal (Zeitschrift für Spiritus-Industrie) but in a complete volume at the close of the year. * * * * In connection with the Kalendar we publish, this presents a complete compendium of the developments of each new year."

Dr. Delbruck has not exaggerated. It is almost a handbook as well as a yearbook, for nearly every operation in the fermentation, starch and starch derivatives industries is discussed with some suggestion for improvement. From the culture of the potato and barley, the production of malt and yeast, the control of the fermentation and distillation processes, to the separation and utilization of the finished products and wastes, each step has had the attention of specialists appointed to study them and the report in each case is full of valuable information. In addition to the reports from the different sections into which the works of the societies is divided, we are offered most interesting stenographic reports of the general meetings. It would be impossible to recapitulate here what is set forth in the book. It is enough to say that it is filled from cover to cover with facts of the highest scientific and practical value.

Dr. Delbruck intimates that the most important development is that "our investigations have given a new interpretation to the views developed by Buchner, that in the life of yeast we must differentiate *protoplasm*—the seat of life—and *enzyme*—the working constituent (Arbeitstoffe)—of the organism. Their prosecution has now developed facts which will be of importance to the fermentation industries and particularly to physiology. The theme is the struggle of the enzyme in the yeast cell."

The book has a value therefore beyond the boundaries of the industries named and while it should be found in the working libraries of all progressive technologists it will be found useful as a source of valuable suggestion to biologists and physiologists in their work. W. McMURTRIE.

A LABORATORY MANUAL OF PHYSICS FOR USE IN HIGH SCHOOLS. By HENRY CREW, PH.D. AND ROBERT A. TATNALL. New York: The Macmillan Company. 1902. xii + 234 pp. Price, 90 cents, *net*.

The authors have certainly succeeded in producing a very commendable book. The experiments have been carefully selected with a view "to illustrate the first principles of physics as simply as possible," and the directions for their performance are so clear and to the point that much teaching energy is saved. Several new experiments are given as substitutes for the classical ones or to illustrate points hitherto somewhat neglected in elementary physics. The number of experiments is sufficient to admit of some latitude of choice, and by means of references the work in the laboratory is brought into close correlation with seven of the best text-books on elementary physics. There are three appendixes, the first being an interesting reprint from a paper by Robert Boyle on "A New Essay Instrument, etc.", published in 1675, the second giving advice as to the selection of a galvanometer, and the third containing various physical constants. C. E. LINEBARGER.

PLATTNER'S MANUAL OF QUALITATIVE AND QUANTITATIVE ANALYSIS WITH THE BLOWPIPE. Translated by HENRY B. CORNWALL, E.M., Ph.D., assisted by JOHN H. CASWELL, A.M. Eighth edition revised after the sixth German edition, by PROF. FRIEDRICH KOLBECK. Illustrated with 87 wood cuts. New York: D. Van Nostrand Company. 8vo. Cloth. Price, $4.00.

All students of blowpipe analysis will be pleased to have this latest edition of Plattner's classic work in their libraries, especially

when they find that its subject-matter has been kept thoroughly up to date through the labors of Professors Richter, Kolbeck, and others and by valuable foot-notes and suggestions of the translator. Although the blowpipe behavior of several new minerals has been added and some lately devised reactions included, no essential alterations have been made. It is accordingly unnecessary to make an extended review of a work which all will admit is unsurpassed and has been proved in the hands of a generation of students.

The book is divided into three sections:

First, "A Description of Apparatus and Reagents" which is fully illustrated and occupies 56 pages. In this section all apparatus and reagents approved by experience are described.

Second, "Qualitative Blowpipe Analysis." This section occupies the major portion of the book and contains 289 pages. It is complete to the minutest detail and besides the simpler blowpipe reactions gives full directions for separating interfering elements. Here, too, will be found the detailed action before the blowpipe of all minerals and metallurgical products which even the expert is likely to be called upon to identify and for this reason alone the book should be found in every mineralogical laboratory.

Third, "Quantitative Blowpipe Analysis" occupies 94 pages. To the blowpipe enthusiast this section will perhaps prove the most interesting. It is, however, probable that the assayer and chemist will for some time to come monopolize this branch of the subject. Its assays for silver, gold, copper, lead, bismuth, tin, cobalt, nickel, and mercury are highly ingenious and will commend the admiration of all chemists for the intricate knowledge of the chemical reactions involved and their application to the end to be attained.

It seems almost presumptuous to make any criticism of a work of this character but many will regret the omission from the translation of the spectroscopic methods, at least as applied to the ordinary flame spectra. These reactions are surely as applicable to blowpipe work as the many wet methods given, and no procedure gives quicker or more certain results. The chemical notation can hardly be called modern as the old dualistic formulas are still applied to by far the larger number of minerals. All, too, will regret the use of such obsolete terms as sesquioxide, protoxide,

bisulphate of potassa, etc. The work of the translator has, however, been admirably done. The German has been intelligently and accurately converted into excellent English and the paper, typography, and binding are first-class.

The book is well indexed. CHARLES LATHROP PARSONS.

AMMONIA AND ITS COMPOUNDS—THEIR MANUFACTURE AND USES. By CAMILLE VINCENT. Translated from the French by M. T. SALTER. London: Scott, Greenwood & Co. 1901. viii + 114 pp. Price, $2.00.

The author, Camille Vincent, is well known for his method of preparing methyl chloride from the vinasse of the beet-root sugar. In this book he has described in some detail the methods used in France for the production of ammonia and the ammonium compounds. So far as it goes the book is well conceived and well written, but it by no means exhausts the subject and is notable for the almost entire neglect of the commercial side—the cost. One of the large sources of ammonia, the English shales, some of which give 72 pounds of sulphate per ton, is not mentioned. Nor is any attention given to the synthetic preparation of ammonia—a problem now apparently nearing solution. EDWARD HART.

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THE LAKE SUPERIOR FIRE ASSAY FOR COPPER.

BY GEORGE L. HEATH.

Received April 24, 1902.

AS THIS method has been practically omitted from the latest editions of Peters' "Modern Copper Smelting," because of the superabundance of metallurgical material of wider interest, and as no full description has been published since the original paper of Mr. M. B. Patch was printed, many years ago, it may be of advantage to students, and to assayers, to place on record the details of present practice in refineries and stamp mills of the Lake Superior district.

The assay is adapted only to native copper occurring in veins, or bedded deposits, including the milled concentrates from the same, and also any oxides, carbonates or silicates of copper, if entirely free from sulphur. While Mr. A. H. Low,[1] of Denver, has been very successful in perfecting the "cyanide" and "iodide" assays of copper ores they are not as well adapted to native copper products[2] as the "electrolytic" assay or the Lake Superior crucible "fire assay."

In the lake region, choice of method is made according to the coarseness and richness of the sample to be treated and the tech-

[1] Peters' "Modern Copper Smelting," latest edition.

[2] *Eng. Min. J.* (1895), pp. 369 and 387.

nical accuracy required. The Heine Blue Test,[1] improved by the writer and others, is suited for rapid working tests of poor slags and tailings under 1.5 per cent. copper. For accurate work on material easily sampled, the battery assay[2] is employed, with special modifications when applied to refined copper.[3]

SAMPLING OF MATERIALS CONTAINING NATIVE COPPER.

The estimation of the metal may be required in:

I. Mine rock, as hoisted from prospecting shafts;
II. Mill concentrates, gravels and tailings;
III. Rich reverberatory furnace slags;
IV. Waste slag from "slag remelting" cupolas.

I. The low grade vein rock of the mines is well understood to carry the metal in particles of such uneven size, so unevenly disseminated in the lode, that any valuation of even a stope on anything short of a mill test of 100 to 500 tons, is of no practical value. An approximate test of any particular carload might be made by crushing to chestnut size, sampling down, grinding several pounds with repeated siftings, picking out and weighing separately the shots left on each sieve, and fusing 0.25 to 1 pound of the remaining fines in a crucible with appropriate fluxes.

II. According to the writer's experience, the "battery assay" of rich concentrates does not give as good results in the long run as the "fire assay," even if a large sample is dissolved in acid and an aliquot part by volume of the solution is taken for the electrolysis. Results would be better if aliquot parts were taken by weight, for the multiplication of slight errors in measuring flasks tends to make the result rather inaccurate.

Rich coarse material can not be accurately sampled for 1000 grain assay, when very dry, but should be wet sufficiently to make the particles adhere and a sample taken out of the material for a water determination, just before the one for copper. At refineries, concentrates are sampled by the furnace men, either at the shutes when filling hand-carts, or from the mixed pile on the charging floor of the furnace, the sample being preserved in tightly covered tin-lined copper cans.

At the C. and H. Stamp Mills, coarse gravels and other non-

[1] This Journal, 19, 24; Smith's method: *Eng. Min. J.* (1900), pp. 307–364.
[2] *Eng. Min. J.* (1895), pp. 369 and 387.
[3] *Trans. A. I. M. E.*, July, 1897.

homogeneous material have been effectively sampled down to a small portion for a "battery test" by the method of repeated siftings with removal of pellets, as suggested for vein rock (I). Some of the larger mills send the concentrates to smelters in steel cars having a cross-section somewhat like an inverted hyperbola while the smaller concerns ship in oil barrels or casks.

To avoid rehandling, the concentrates of each grade are often sampled in the cars or other containers, just before weighing, by means of a pointed tube with a slit on the side, something on the principle of the cheese tryer. This instrument seems to drive back the water a little and produce a sample that is a little too dry, and therefore a little too rich in the red metal. As the percentage of moisture continually varies in all mill products, it is necessary in all comparative work to calculate assays to dry weights of material.

Principle of the Fire Assay.—The ideal would be attained, if one could succeed in melting and reducing all the copper in a sample by fifteen or twenty minutes' fusion in a pot-furnace, without carrying any iron into the button, to be incorrectly weighed as pure copper. In practice it is found that we can so flux and fire native copper concentrates (over 40 per cent. copper) that the loss of copper in the slag can be kept at about 0.25 per cent. (of the mineral weighed) and shall be balanced by iron in the copper button, equivalent to 0.25 per cent of the original sample. It is also possible to tell, by the eye, the purity of the copper button, and the waste in the slag, within a limiting error of about 0.1 per cent. either way.

With low grades of mineral and slags, the correctness of the assay can not be told so closely by the appearance of button and slag, but a button entirely free from iron can be distinguished from one carrying enough to affect the assay result 0.1 per cent. or more. Accordingly, some laboratories fire low grades (5 to 30 per cent. copper) with such a fluxing and reducing mixture that no iron shall be carried into the button. The copper lost in the slag (usually 0.3 to 0.4 per cent.) is quickly estimated with sufficient accuracy by calculating roughly the weight of slag produced (according to formulas to be given), crushing a portion, estimating copper by blue test, and adding the total weight of copper found in assay slag to the weight of the button.

Check assays should always agree on rich grades within 0.2 to 0.4 per cent., and on poor grades within 0.2 per cent. From month to month, the fire assay, when properly conducted at a smelter, should check the output of the reverberatories, adding the slight loss in the waste slag from the cupolas.

A large assay button from rich material should be bright on all sides and have a small hole in the top with wavy or rough upper surface surrounding the cavity. A very smooth button and red slag indicates undue slagging off. If the large button has no hole and is dark on the bottom, except possibly a slight ring or film of brown on the outer edge, it will be too high in iron. Small buttons from low grades should be bright, and smooth, or with striations on upper surface, but no cavity.

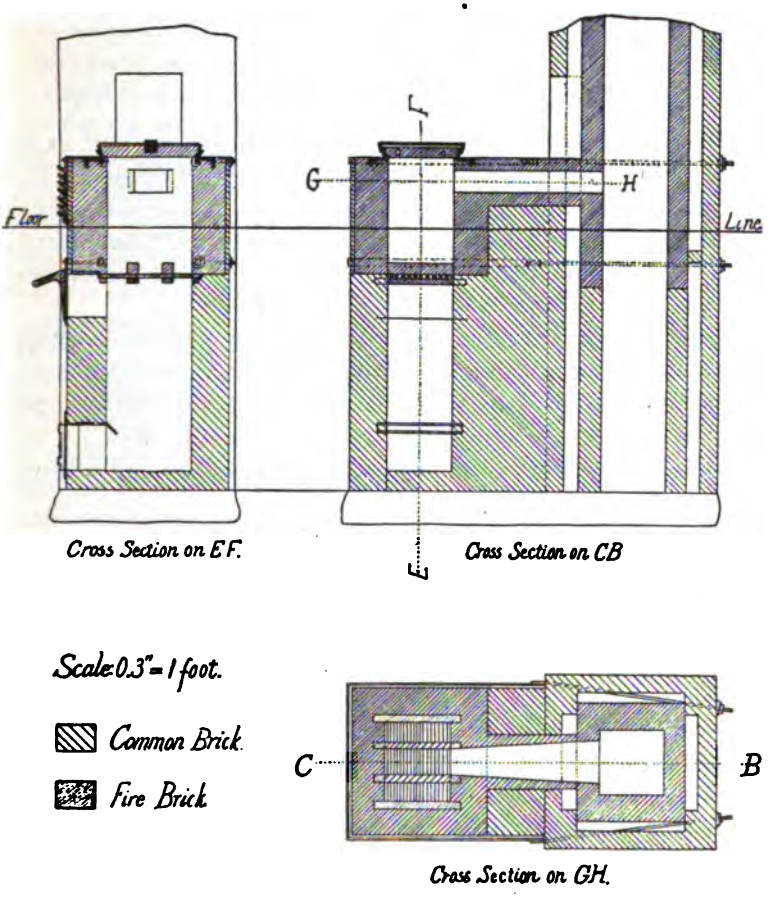
Pimples and pits, or a purple film on such a button are produced by sulphur, or by fragments of coal having dropped into the crucible. The slag from rich material (over 40 per cent. copper) should be colored black, or dark brown,—from low grades, black, or nearly so.

APPARATUS AND FUEL.

A pot furnace, similar to the accompanying illustration, is generally employed, but a much higher temperature and quicker heat is required than can be attained with coke and natural air-draft in twenty-minutes' time. To secure the quick, sharp heat, the furnace and stack must be brought to a high temperature before charging the crucibles, by egg-size soft coal and natural draft or by coke with an air-blast under the grate.

At the new laboratory of the C. and H. Stamp Mills, the blast produced by the smallest size Root blower is passed through a 2-inch galvanized iron pipe, to the air-tight ash-pit of the furnace. Two rows of fire-brick (2.5" × 2.5" cross-section) are placed across the grate, and the fuel is kept at least 2 inches above the top of these.

The mill of the Mass Mining Company is said to have installed a furnace pot heated with air-blast gasoline burners, which may be very satisfactory for a small plant. Rich grades melted in sand crucibles require a quick, sharp heat. Low-grade stuff, if fired in Denver clay crucibles, requires that the heat should be lowered to cherry-red just before charging, and that part of the soda be



placed on top of the charge in the crucible. These precautions are taken to prevent pellets sticking to the inside walls of the crucible.

Not only different classes of material, but the same grades, if fired in different makes and styles of crucibles, will require considerable changes in fluxes, especially in the reducing agent—cream of tartar. Crucibles of Denver clay, or of sand, affect the slag in a manner similar to the action of "basic," or "acid" linings in Bessemer converters. The more basic Denver crucible with round top and tightly fitting cover requires more flux and far less reducing agent, than an open-shaped triangular sand crucible. The latter is better to keep iron out of the large copper buttons

from rich material, while the Denver clay with extra thin walls has proved better for low-grade silicious stuff.

THE ACTUAL ASSAY.

Fluxes.—The cream of tartar must be 99.5 to 100 per cent. pure, and all the chemicals must be free from sulphur or sulphates. For soda, it has been found advisable to buy the "Natrona brand" sodium bicarbonate, which is fused in a large iron ladle, poured into a smooth iron dish, or ladle, to cool, and then pulverized through a sieve of 20 meshes to the linear inch.

Refined crystallized borax is fused in a Dixon graphite crucible, poured into an iron dish and pulverized to pass a 20-mesh sieve. Powdered silica is occasionally employed for very ferruginous slags, such as blister slag, and powdered hematite (Fe_2O_3) for very silicious material, such as gravels, or carbonates and silicates of copper.

Weighing.—The moist material is dumped by the assayer on a sampling board about 15" x 20" in area. Operators formerly used a tray made of straight-grained wood, which has to be wet with water frequently and the superfluous moisture removed with a cloth. The best thing, in every way, that we have used is a vulcanite tray, 15" x 19" in size, such as is sold for photographic purposes. The long side of the tray next to the operator is cut out, and we have a sampling platform which does not absorb moisture, and does not break or wear out with months of use.

The assayer quickly mixes the sample with a large steel spatula, and covers up the pile which is then pushed outward from the center and flattened to a layer about 1 inch thick and 1 foot square, or a little more. With a steel spatula (8-inch blade), vertical slices are quickly taken at regular distances apart (generally from 9 equi-distant points), dipping to the tray each time in such a manner as to make up 1000 grains on the pan of the pulp balance. This first sample is put in a dish or can, to be dried for the estimation of water, and a second portion is immediately taken for a copper assay and placed on oiled or smooth white paper.

Mineral containing 70 to 95 per cent. copper makes so little slag of itself and needs so little flux, that there would not be enough from the gangue present, to cover the button and keep it deoxidized while cooling. On this account a large stock of old assay

slag is accumulated, preferably from low grades, ground to pass a 20-mesh sieve, assayed for copper, and a certain quantity added to each crucible charge of rich material to act as a regulator and a cover for the button. If known grades, varying within narrow limits, are regularly assayed, a large quantity of complete fluxing mixture can be made up and added by measure instead of weight. Otherwise, weigh fluxes roughly, according to formulas determined by experience, mix with the spatula, transfer to crucibles and add a cover $^1/_{16}$" to $^1/_8$" deep of cream of tartar.

Scrape away the hot coals from the surface of the rows of brick in the furnace, close each crucible when in position, with a clay cover to keep out coal, poke the hot fuel around the crucibles, and fill in fresh coal (egg size) up to 1 inch below the top of the sand crucibles, or a little higher for Denver clay crucibles. The covers can be made in wooden molds from a mixture of fire-clay and ground fire-brick. Old crucible bottoms luted with clay could be employed. When using soft coal, the writer has the fire poked gently in from five to seven minutes from the start (according to the sharpness of the heat) coaled lightly in four minutes more, poked again five minutes later, and the assays taken out two to three minutes afterwards, the furnace having come to a very high heat —total time sixteen to eighteen minutes. Leave any charge not melted, until it just comes to quiet fusion. The melts should not be jarred while cooling. The success of the assay depends largely on the quick and sure regulation of the time and degree of heat.

The above manipulation is for soft coal and a double-walled tight furnace. Coke, or gasoline fuel, would require different manipulation to get the same results in the time allowed (in general not over twenty minutes for complete fusion). If low grades are to be fired in Denver "E" crucibles, the furnace and stack should be thoroughly heated, but the grate cooled down to a bright red by taking the furnace cover off for a few minutes just before firing the assays. The heat can be brought up within the time allowed, but the slower start helps to prevent pellets from sticking to the crucible.

Specimen charges are here given to show the average weights which each flux loses in melting down, and thus to indicate a method by which any one can approximately calculate what total slag will be produced in any case, and, in conjunction with the

colorimetric assay of that slag, the total copper slagged away from the button.

SMALL NO. 5 HESSIAN TRIANGULAR CRUCIBLES.

Composition of charge.	Losses in melting deducted. Per cent.	Calculated slag produced. Grains.
Rich mill concentrates, sample = 1000 grains.	$(Cu + H_2O) = 88$	120
70 to 50 grains sodium carbonate.....	40	42
70 to 50 grains borax glass.....	0	70
250 grains assay slag (0.3 per cent. copper)..	0	250
300 grains cream of tartar.....	75	75
Total slag		557

Actual weight of slag found to be 550 to 570 + grains.

SMALL NO. 5 HESSIAN TRIANGULAR CRUCIBLES.

Composition of charge.	Losses in melting deducted. Per cent.	Calculated slag produced. Grains.
Poor (slime) mineral, 1000 grains.....	$(Cu + H_2O) = 33$	670
150 to 200 grains sodium carbonate	40	90
150 to 200 grains borax glass.....	0	150
350 grains cream of tartar	75	88
Total slag		998

Actual weight varies from 1000 to 1025 grains.

As the only appreciable impurity of copper assay buttons is metallic iron, if we desire an exact assay on any unknown sample, we have only to determine the iron in the button and the trace of copper lost in the slag, calculate both results to the 1000 grains of mineral tested, and apply the corrections to the weight of the button. This calculation will furnish also a guide as to the effects of experimental variation of fluxes and conditions of heat.

Specimen charges employed in practice at lake refineries are presented in the following table. They are based on the original paper of Mr. M. B. Patch and on the later experience of the writer and assistants with a variety of material.

It will be advisable to use the higher limiting quantity of soda on rich concentrates, when the old assay slag employed has been preserved from 1000 grain assays of low-grade material only, as such slag is proportionately lower in soda and oxide of iron than the usual slag produced years ago. Conglomerate mineral contains much more ferric and titanic oxides than the amygdaloid. In all cases there is some fine metallic iron in mill products, due to the wearing of the stamps.

COMPOSITION OF FLUXES.

Class of material.	Source.	Usual limits of Cu.	Limiting per cent. of water.	Make of crucible.	Weight of sample. Grains.	Fluxes—all weights in grains. Cream of tartar.	Fused soda (Na_2CO_3).	Borax glass.	Old assay slag.	Iron ore (Fe_2O_3).	Sand (SiO_2).	Time in minutes.
[1]Mill products, rich concentrates.	Conglomerate.	90–70	1–5	H or B	1000	300	50–150	50	250			15–17
[2]As above only much coarser.	Amygdaloid.	95–75	0.5–3	H or B	1000	300	150	50–40	250			16–18
				Denver "G"	2000	300	250	100	350–375			17
Medium grades.	Conglom. or amygdaloid.	70–40	5–10	H or B	1000	300	100–150	100–150			0–100	
[3]Lean grades, table stuff, etc.	Conglomerate.	30–10	10–20	B or H	1000	300–350	150–250	200		0–50		16–18
				B or H	500	300	150–200	150–200				17
				D	1000	200	150 on top of charge. 200 mixed in.	300		0–50		16–17
[3]Lean grades, table stuff, etc.	Amygdaloid.	30–10	10–20	B or H	1000	300	200–250	200		50		16–20
				D	1000	200	150 on top. 225 mixed in.	375		0–50		16–18
[4]Reverberatory slags.	From mill concentrates.	25–10	0	B or H	500	300	200	200				18–20
				B or H	1000	400–450	320	320				20
				D	1000	350	400	400				16–20
[4]Reverberatory slags.	From melting rock, barrel work.	25–10	0	B or H	500	350	200	200		100		16–20
				B or H	1000	450	350	350		200		18–20
				D	1000	360	400	400		200		16–20
Blister furnace slag.				B or H	1000	300–400	300	300			150	17–20
Lean gravels and silicious ore.		5–10		D	1000	350+	400	400		50–100		17–20
Copper and iron oxides.	Surface ores, no sulphur.			H or B	1000	350–400	300	350			50–150	17–20

[1] Quick heat. • Increase cream of tartar for black oxidized stuff.
[2] Best assay for very coarse Cu.
[3] Low grades average more silicious than years ago.
[4] Ground to pass 20-mesh sieve. Coarse shot picked out and weighed separately.

B = U Battersea Δ-shaped top.
H = Small 5 Hessian Δ-shaped top.
D = "E" special thin wall, Denver clay, O shape.

It is evident, from the foregoing description, that the Lake Superior fire assay bears no relation to the empirical matting assay in use at Swansea, but is a practical method, easily controlled when once thoroughly learned, and sufficiently accurate for all technical purposes.

NOTES ON THE ESTIMATION OF COPPER BY POTASSIUM PERMANGANATE.

By H. A. Guess.

Received April 25, 1900.

ALTHOUGH at various times, during the past few years, different chemists have proposed the use of an alkaline thiocyanate as a precipitant in the estimation of copper,[1] and although the results have been shown to be sufficiently accurate for technical purposes, the fact remains, that the method has made little headway, in competition with the electrolytic, cyanide, or iodide methods, in technical work, particularly in the metallurgical laboratories of the West, where the iodide method is greatly in favor.

In the iodide method, as generally practiced, the copper is first precipitated by aluminum strips, and while this precipitation is fairly rapid and complete in concentrated solutions, it is not at all so in dilute solutions of 20 milligrams or less of copper in a bulk of 150 cc. of dilute sulphuric acid. Furthermore, other metals, particularly arsenic, interfere by being precipitated along with the copper, and have to be rendered inert by oxidation with potassium chlorate. On the other hand the precipitation of copper as thiocyanate is practically complete at the moment of adding the precipitant; no other metals interfere, silver being the only other metal precipitated by an alkaline thiocyanate from an acid solution, and its thiocyanate is unacted upon by the subsequent caustic alkali treatment.

It has seemed to the writer that the main drawback to the method as so far proposed is the use of asbestos as the filtering medium, and the consequent necessity of filtering-pumps, which in a laboratory doing 100 or more copper assays in a day would render the process awkward and cumbersome. For the past six

[1] This Journal, 20, 610; 22, 685, *et seq*; *Am. J. Sci.*, 163, 20-26; *Chem. Centrbl.*, 1, (19), 1085 (1899).

months the writer has used a modified form of this process, for the estimation of copper in ores, tailings, and concentrates, doing away with asbestos as filtering material, and using filtering paper well extracted (with hydrochloric acid and hydrofluoric acid) instead, the process being briefly as follows:

From 1 to 5 grams, depending on the material for assay, are digested in an 8-ounce flask with nitric and hydrochloric acids, together with a few drops of sulphuric acid, to get rid of any lead present, the excess of acid is boiled away, the acid solution diluted, filtered, and the residue well washed on the filter. The acid filtrate is neutralized with ammonia, and then rendered just acid by a few drops of dilute hydrochloric acid; the acid cupric solution is reduced by an excess of sodium sulphite, or sulphurous acid previously nearly neutralized by sodium carbonate, and the copper precipitated as white granular cuprous thiocyanate by a slight excess of potassium or ammonium thiocyanate. The mixture is heated to boiling, the precipitate settling rapidly; the clear supernatant liquid is decanted through an 11-cm. filter, and the residue, after washing by decantation, is finally washed upon the filter, and thoroughly washed with hot water. The funnel, with its filter and precipitate, is now placed in the original precipitation flask, and a boiling 10 per cent. solution of caustic soda poured through. The operation is repeated with a further amount of the caustic solution, the filter being filled full each time to insure complete contact with all of the precipitate. Complete decomposition of the cuprous thiocyanate takes place, the equation being $CuCNS + NaOH = CuOH + NaCNS$; the insoluble yellow cuprous hydroxide remains on the filter, the alkaline thiocyanate passing through. The filter and contents are well washed with hot water, the alkaline filtrate made decidedly acid with dilute sulphuric acid, and the liberated thiocyanic acid titrated with standardized potassium permanganate at the warm temperature given to it by the hot water washings.

This method, like most other technical ones, is not perfect. The chief imperfection lies in the slight solubility of cuprous thiocyanate in the solutions present. Careful experiments as to this solubility have been made by testing the filtrate and washings from the precipitation, as thiocyanate, of weighed amounts of pure copper; the copper in solution in the filtrate is determined colori-

metrically by potassium ferrocyanide, and also by formaldoxime[1] (prepared by mixing 20 per cent. formaldehyde solution with an equimolecular proportion of hydroxylamine hydrochloride), the reaction being an intense violet coloration for the faintest traces of copper. It was found in this way that the most complete precipitation of the copper was obtained when made under the conditions above outlined, and even under these conditions the precipitate is to a slight extent soluble, the degree of solubility being most accurately determined by standardizing potassium permanganate solution with pure copper as above described, and comparing the value thus obtained with the copper value calculated from the carefully determined iron value of the same solution. Thus, comparing the equation

$$10HCNS + 12KMnO_4 + 8H_2SO_4 = 6K_2SO_4 + 12MnSO_4 + 10HCN + 8H_2O$$

for thiocyanic acid and permanganate with the iron equation for permanganate, the copper-iron ratio is 10Cu:60Fe and the factor for copper from the iron value is 0.1892. The copper value, as determined by the precipitation (as thiocyanate) and titration, represents a factor of approximately 0.192 of the iron value, the difference between the two being due to the slight solubility of the cuprous thiocyanate and the consequent incomplete precipitation.

By standardizing the permanganate solution always against pure copper, under the same conditions as the regular assays, this error of solubility is for all technical purposes eliminated. The other imperfection of the method is the action of the filter-paper on the hot caustic alkali solution, which is very slight, and is constant for the same type of filter. It can be ascertained by running a blank filter under similar treatment, titrating, and making the correction. On an 11-cm. filter, it amounts usually to 0.3 cc. potassium permanganate, of a strength of 1 cc. equal to 2 milligrams copper.

The method has been run in parallel with the iodide on the same samples in this laboratory during the past six months, in daily assays of concentration-mill products, and in 'control' assays on smelter shipments, some 3000 determinations having been made by the method in that time. The method was begun in

[1] A. Bach: *Compt. rend.*, 128, (6), 363-365.

a tentative way at first for tailings assays, for which neither the cyanide nor iodide methods were suitable, nor, from the arsenic and manganese present, was the usual colorimetric method. It was later adopted for the assays on crude ore and concentrates, and its results have been uniformly satisfactory. In practice it takes about the same time as the iodide method, and while, for copper to the amount of 3 per cent. and upwards, it may not offer many advantages over the latter method, which cannot well be improved upon, it is more accurate than, and distinctly superior to, either the iodide or cyanide method for small or fractional percentages of copper.

LABORATORY OF THE SILVER LAKE MINES,
SILVERTON, COLO., April 19, 1902.

[CONTRIBUTION FROM THE LABORATORY OF THE BUREAU OF INTERNAL REVENUE, U. S. TREASURY DEPARTMENT.]

THE INFLUENCE OF THE GROWTH OF MOLD UPON THE CHEMICAL COMPOSITION OF OLEOMARGARINE AND BUTTER.

BY CHARLES A. CRAMPTON.

Received April 12, 1902.

HAVING occasion to pass through the ordinary course of analysis a number of samples of oleomargarine, which had been kept in glass-stoppered bottles for about two years, I was much surprised at the results obtained. The samples, about fifty in number, had a well-authenticated history of having been taken from different packages of the same shipment of oleomargarine, a shipment which was represented by a single sample taken at the time and examined in this laboratory, giving a normal Reichert-Meissl figure.

Instead of obtaining the usual figures from the fifty old samples, as would be expected, and a close agreement among themselves, the results varied greatly; and what was still more striking, the figures given by one determination—that of the refractive index—were so low in some cases that the samples would have been classed as butter, if judged by this test alone, while others gave results normal for oleomargarine. Many of the samples were permeated with a growth of dark green mold, and on tabulating the results, it was soon seen that this was the cause of the differences, the

greatest divergence being between the samples showing a strong growth of the parasitic plant, and those showing a little or none.

The samples were divided roughly into three classes, according to the apparent amount of mold present.

Unfortunately, the amount of material was very small in any of the samples, so the only determinations that could be carried out upon all were of the Reichert-Meissl figure and refractive index, but specific gravity, Valenta, and iodine values were obtained from a few samples in each class.

The average figures for each group are tabulated together, as follows:

Group.	Reichert-Meissl value.	Refractive index at 25° C.	Specific gravity at $\frac{25°}{15°}$.	Valenta value.	Melting-point.	Iodine value.	
1. (19 samples)	4.77	1.4646	0.9084	77.00	45°	44.28	No mold.
2. (20 samples)	3.82	1.4633	0.9080	36.5	45°	43.66	Slightly molded.
3. (9 samples)	2.98	1.4610	0.8979	31.0	45°	49.81	Heavily molded.

It will be seen that the molded fat gives a much lower average figure in all the constants than the fat free from fungus, with the single exception of the iodine value. The melting-point is the same in all. The original sample which represented the same material, and which had been kept in this laboratory since December, 1899, was looked up and found to be apparently free from mold. It is not strictly comparable with the series of samples which were taken and preserved by parties other than internal revenue officers, but may fairly be presumed to approximate pretty closely the same material. Unfortunately but one determination, that of the Reichert-Meissl value, was made upon this sample at the time of its receipt in 1899. It gave R. M. = 2.42. An ample supply of material was still available which had no outward appearance of change, except that it had developed the tallowy smell incident to oleomargarine on long keeping.

Following are the results obtained:

SERIAL NO. 5264.

Specific gravity at $\frac{40°}{40°}$	0.9105
Refractive index at 25° C	1.4647
Reichert-Meissl value	4.86
Acid value (cc. normal alkali required for 100 grams fat)	17.10
Hehner value	92.70
Valenta value	68.0
Crismer value	66.3
Iodine value	47.52
Soluble fatty acids, per cent	1.04

These results correspond pretty closely with those obtained on the samples which showed no mold. Taken together, they indicate a very decided change in the values of the fat on long keeping, much more than has usually been recorded for butter-fat. The only determination made on the original, the Reichert-Meissl value, gives a considerable increase, and the other values have doubtless also changed, as some of them are quite abnormal for oleomargarine.

The figures obtained from the molded samples show a very wide divergence from the values given by those which have, presumably, been affected only by the action of the atmosphere. The Reichert-Meissl figure is much less, approaching the value ordinarily obtained from fresh oleomargarine, while the refractive index and Valenta value are about normal for butter. The specific gravity is very low, even lower than the normal figure for oleomargarine, and far below the specific gravity of the rancid samples. The iodine value shows a remarkable variation, which may be partly due to some difference in the original composition of the samples. Some of the latter gave a reaction for cottonseed oil, while others did not. The mold occurred in black spots on the fat, which penetrated entirely through the mass. The fat, on filtration, was of a reddish brown color, quite different from the color of the fat from the samples free from mold. In other respects (odor, taste, etc.) they did not differ greatly.

The samples, or rather *residues* of samples, had been kept in glass-stoppered wide-mouthed bottles. Several of the bottles were sent to Dr. Erwin F. Smith, of the Bureau of Plant Industry of the U. S. Department of Agriculture, who had kindly agreed to determine the character of the mold. He reported as follows upon the result of the examination: "All of the oleomargarine bottles furnished by you containing fungi have now been examined. The

bulk of the black substance in each one is *Coniothecium*, probably an undescribed species. The species of this form-genus are not well differentiated, and are generally named after the substratum on which they are found. So far as I know there is no record of any such fungus on butter. *Aspergillus* occurs sparingly in three of the bottles, 5058, 5060 and 5061, but not in the fourth, 5014, and I cannot bring myself to believe that it occurs in sufficient quantity to have had any influence on the oleo."

Efforts to engraft this mold upon butter have, thus far, proved unsuccessful.

On making a search of the journals for recorded observations on the effect produced by mold on the composition of fats, I found the work of Hanus and Stocky: "Ueber die chemische Einwirkung der Schimmel-pilsen auf die Butter" (*Zeitschrift Unt. Nahr. und Genussmittel*, (1900), 3, 606).

They found that a sample of butter which had become covered with mold gave, on analysis, figures differing considerably from those originally obtained, more especially in acidity and volatile acids. They then made pure cultures of nine different species of mold and engrafted them upon butter of known composition. After three months had elapsed, they found very little change, which they explain upon the theory that the molds attack primarily the milk-sugar and protein substances in the butter, and first exert their effect upon the fat after these have been consumed. Finding that the species *Mucor mucedo* was best adapted to their purposes, on account of its mycelium penetrating deeper into the butter than the other varieties, they engrafted a culture upon butter of known composition, and allowed it to develop for a year, carrying along with it a blank sample of the same butter free from mold.

I have collected their results upon the three different samples into the following table:

Chemical constants.	Original butter-fat.	Blank control sample.	Molded sample.
Acid figure (cc. normal alkali required for 100 grams fat)	5.10	107.0	109.5
Reichert-Meisal figure	27.17	24.3	24.0
Saponification figure	226.00	222.1	217.3
Iodine figure	36.20	34.1	35.2
Volatile acids, per cent	5.10	4.96	4.90
Molecular weight of volatile acids	93.70	102.1	102.2
Free volatile acids, per cent		0.40	0.55
Molecular weight of free volatile acids		154.0	144.0
Ether figure		162.2	156.3

From these results they reach the conclusion that the growth of molds has a decided effect upon the composition of butter-fat, splitting up the glycerides into fatty acids and glycerol, the latter serving as a nutrient to the molds; secondarily, the free fatty acids of lower molecular weight are either oxidized to higher acids, or are reduced, the presence of aldehyde-like bodies favoring the latter hypothesis.

The original butter used in the experiment was not sterilized, and the authors noted a considerable development of *oidium*, a different type of fungus growth, in the control sample, and also in the sample engrafted with *mucor*, both species growing together. They are, therefore, unable to say just how much of the change in composition is due to the growth of *mucor*, how much to *oidium*, and how much to the action of air and light solely.

Laxa[1] found that the molds, *Oidium*, *Penicillium*, and *Mucor*, effect a hydrolysis of butter-fat, as do also the yeasts, though to a less extent. I have no access to the original paper.

The most recent and conclusive work upon the fat-destroying power of molds is that by Koenig, Spiechermann and Bremer,[2] whose paper contains also a comprehensive review of the results recorded by other observers in this direction. They investigated the changes produced in the composition of cottonseed meal, along with other food and fodder materials, by various classes of micro-organisms. They found a well-marked effect exerted upon the oil by both bacterial and fungous growths, under conditions favoring their development. I will quote here the more pertinent of their conclusions:

"8. Experiments with pure cultures of *mycelium* fungi obtained from cottonseed meal, and with other species grown upon sterilized cottonseed meal, and also upon artificially prepared nutrient material containing fat, have shown that the *mycelium* fungi are abundantly able to use as a source of carbohydrate both fats and the higher fatty acids (liquid and solid).

"9. Hand in hand with fat consumption goes always the splitting up of the fat, yet this reaction never extends to the entire body of fat present, and it varies in strength with different micro-organisms.

* * * * * * *

[1] *Arch. Hyg.*, 41, 119; *J. Soc. Chem. Ind.*, 21, 268 (1902).
[2] *Zeitschrift Unt. Nahr. und Genussmittel* 4, 721 and 769 (1901).

"11. The fat is apparently, for the greater part, decomposed directly into carbonic acid and water."

The investigation showed that bacteria resisting a sterilization temperature of 100° (so-called *kochfester* bacteria) were capable of bringing about the decomposition of fat, though not to the same extent as the fungous growths which are visible to the eye.

The results obtained by me strengthen the conclusions reached in the investigations outlined above, and have two important bearings:

First, a most practical bearing upon the interpretation of analytical results; and second, upon various unsolved problems of the constitution and metamorphosis of the glycerides. In regard to the first, the obvious lesson is that no reliance can be placed upon the ordinary constants used for the detection of foreign fats in butter when the sample in question has been invaded by the growth of mold. An *apropos* instance may perhaps be cited in a communication by H. Droop Richmond in the *British Food Journal*, (1903) 3, 393. The writer discusses the anomalous results obtained in the analysis of Russian butter in certain important legal cases before the English courts. He is unable to account for the figures obtained, some of which point strongly towards adulteration; but he mentions, incidentally, the fact that his samples showed the growth of a mycelium fungus, and this probably affords the key to a solution of the entire matter.

A sample of butter, recently brought to this laboratory, showed a growth of mold upon a portion of its surface. A separation of the molded and unmolded portions was made, and the following values obtained. The identity of the mold was not established.

SERIAL NO. 5109.

	Without mold.	With mold.
Reichert-Meissl value	26.79	25.53
Refractive index at 25° C	1.4596	1.4594

These results confirm the observations of Hanus and Stocky to the effect that the growth of mold in butter produces a slight but distinct decrease in the Reichert-Meissl value.

From another sample, however, I obtained values which showed a much more radical change in composition, and which are, so far as I am aware, the lowest in some respects ever reported from a genuine butter. This sample, Serial No. 5385, was received in

February, 1899, at which time it gave a Reichert-Meissl value of 29.92. For some reason it had not been thrown out, and when examined in March, 1902, after remaining three years undisturbed in a tin can, it was found to be thoroughly permeated with a reddish brown mold.

This was examined by Dr. Smith, who reports it as *Coniosporium sp.?* He found also *Penicillium sp.?* in small quantity.

A fair quantity of the filtered fat was obtained, which was of a rather deep shade of orange-yellow. It gave the following values:

SERIAL No. 5385.

Specific gravity at $\frac{40°}{40°}$	0.8978
Refractive index at 25° C	1.4578
Reichert-Meissl value	13.09
Acid value (cc. normal alkali required for 100 grams fat)	141.75
Iodine value	40.66

The Reichert-Meissl value is less than half of the original; the refractive index is abnormal, being lower than that obtained from butter; and the specific gravity is rather lower than the usual "oleo" figure.

Returning to the results obtained from the oleomargarine which had been kept a long time, but which showed no apparent growth of mold, Serial No. 5264, the values approach figures normal for butter, as is also the case with those samples in the series which showed little mold. In further confirmation of this, three other samples of oleomargarine were selected, none of which showed visible evidence of the presence of mold. These samples were received during the months of February and March, 1899, and had consequently been kept (in tin cans) over three years. The following table gives the Reichert-Meissl values at the time of their receipt, and at the time of their re-examination; also the refractive indices, specific gravity, and acid values.

		1902.			
Serial No.	1899. Reichert-Meissl value.	Reichert-Meissl value.	Refractive index.	Specific gravity at $\frac{40°}{40°}$	Acid value (cc. normal alkali required for 100 grams fat).
5386	3.30	4.26	1.4639	0.9102	43.8
5387	1.76	5.60	1.4656	0.9159	5.0
5388	2.20	5.26	1.4679	0.9144	6.1

The changes brought about in the Reichert-Meissl values are fully as radical as in the other samples; the specific gravities also, while no comparison can be made owing to lack of data on the samples as originally received, have manifestly increased, as they are as high as butter normals.

From an analytical standpoint, these changes in composition are even more dangerous than those produced by the growth of a micro-organism like mold which is visible to the eye. That they are due entirely to the ordinary action of air and light cannot be believed, and this leads up to the consideration of the theoretical bearing of the results, particularly upon the nature of rancidity changes. Most of the authorities on fats and oils (Lewkowitsch, Wright, etc.) accept as conclusive the results of Ritzert[1] who found that pure lard was not turned rancid by bacteria introduced into it, as they soon died; and that fat sterilized at 140° became rancid on subsequent exposure to light and air.

I am not now in a position to oppose specifically the conclusion that a fat cannot become rancid without the presence of micro-organisms, although I hope to be able soon to repeat the experiments of Ritzert upon this point. But I do not think there can be any room for doubt that the growth of micro-organisms plays a highly important rôle in the changes which occur in fats and oils under ordinary conditions of exposure. Even if it be granted that the breaking up of the glycerides may eventually take place merely from the presence of oxygen, it is certain that the change is greatly promoted and expedited by their development.

I think it may safely be asserted, for the edible fats, at least, where the presence of nitrogenous and other non-fatty matter affords a sprouting medium for such growth, that the greater part of the changes embraced under the general term "rancidity" is due to the action of micro-organisms, or to the enzymes resulting from their development. The most rational explanation of the results obtained on the samples of oleomargarine appears to me to be as follows: The glycerides, exposed to the cool damp air of the refrigerator, and in contact with the nitrogenous matter derived from the milk used in the process of manufacture, underwent a gradual decomposition, probably induced and promoted by bacterial growth, with the formation of the lower fatty acids. This pro-

[1] *Untersuchungen uber d. Ranzigwerden der Fette*, Inaug. Diss., Berlin, 1890.

gressed to a very considerable degree, giving the high results obtained for volatile acids and specific gravity obtained from the samples which showed no mold. The germs of the *Coniothecium* fungus having gained access to the fat, or, more probably, having been contained in it originally, and their growth being started by the favorable conditions resulting from the splitting up of the glycerides, attacked the liberated fatty acids and glycerides, and consumed them in proportion to the growth. The growth of the fungus produced further decomposition and a further consumption of fatty acids, with a preferment for those of lower molecular weight, until the remaining mixture of fat and free acids gave the diminished values for volatile acids and specific gravity obtained from the molded samples.

Experiments are now in progress in this laboratory having the object of a more exact investigation of the changes brought about in fats by the growth of mold. This I hope to accomplish by growing pure cultures upon a large quantity of fat of known composition. As these experiments will necessarily require a long time for completion, I report the results set forth above as a preliminary paper.

My thanks are due to Mr. F. E. Simon and Mr. A. B. Adams of this laboratory, by whom the principal part of the analytical work was performed.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 65.]

AN ELECTROLYTIC STUDY OF PYRORACEMIC ACID.[1]

BY GEORGE W. ROCKWELL.

Received March 12, 1900.

WISHING to study the effect both of the oxidizing and reducing power of the electric current upon an organic body, aiming at the same time to fix the conditions so that other persons upon repeating the experiments might well expect to get similar results, I selected pure pyroracemic acid for my investigation.

The apparatus employed in the experiments consisted of a beaker glass, a porous cup, which served as a septum for the separation of the anode and cathode liquids, and two platinum

[1] From author's thesis for Ph.D. degree, 1900.

electrodes of 100 sq. cm. surface each. When hydrochloric acid was used as an electrolyte, an anode of carbon was substituted for that of platinum. In several instances lead electrodes were used; these were of the same surface as that of the platinum electrodes.

The solvent generally employed was ordinary alcohol (about 95 per cent.). The concentration of the solution electrolyzed depended upon the conditions assumed for each experiment.

When a temperature sufficient to volatilize alcohol was used, a return condenser was inserted into the neck of the porous cup, by means of a large rubber stopper.

The current employed in most of the experiments was from an ordinary 110-volt incandescent light circuit, which was adjusted by means of lamps and wire resistance frames, so that a current ranging from 0.1 to 10 amperes could be used. Sometimes the current from five chloride accumulators, and in one instance only, that of eight gravity cells of the ordinary type was applied.

The temperature was taken with an ordinary thermometer. The readings were made with the thermometer inserted in the cathode liquid.

Attempts were made to estimate the various products of the electrolysis quantitatively, but I am convinced that they have fallen short in every case.

EXPERIMENTAL PART I.

The experiments considered in this part are those in which the oxidizing action of the current was studied.

A. Oxidation in Sodium Hydroxide Solution.

Experiment 1.—This was conducted with the following conditions:

Pyroracemic acid	5.56 grams.
Sodium hydroxide	10 grams.
Alcohol	100 cc.
Temperature	Ordinary.
Time	22 hrs.
Normal density, N. $D._{100}$	1.3 amperes.
Voltage	$3^3/_8$ volts.

Water sufficient to dissolve the sodium hydroxide was also added.

A Bunsen voltameter containing alkali was inserted in the cir-

cuit, in order to compare the volumes of the electrolytic and experimental gases given off in the same period of time.

One comparison was made and the experimental gas analyzed. The results of the analysis are as follows:

Volumes of the gases disengaged in the same time:

Electrolytic	79.1 cc.
Experimental	12.4 cc.
The experimental gases were	0.4 cc. CO_2
	2.8 cc. O
	9.2 cc. N

This analysis shows the presence of air and as the experimental gases evidently did not escape fast enough to prevent the air from entering in at the joints of the apparatus during the time of their collection, no more comparisons were made.

Toward the close of the experiment it was noticed that the brilliancy of the incandescent lamps, through which the current was conducted, was greatly diminished, until finally the filaments became dull red in color. This indicated that the solution in the porous cup had become greatly deficient in its power of conductivity, but the real cause of this behavior was not noticed at the moment.

The contents of the porous cup were poured into a beaker glass, where they were discovered to have changed color, passing from a straw-yellow to a cherry-red. The solution was allowed to stand over night and then was filtered through a coarse filter-paper to remove silica, after which it was distilled over a free flame. The distillate possessed an ethereal odor.

Experiment 2.—The oxidation was made with:

Pyroracemic acid	4.33 grams.
Sodium hydroxide	5 grams.
Alcohol	50 cc.
Time	$5^1/_2$ hours.
Temperature	Ordinary.
N. D_{100}	1.3 amperes.
Voltage	$3^1/_8$ volts.

Water sufficient to dissolve the sodium hydroxide was also added. In this experiment the experimental gas was collected after the current had been allowed to act for some time. It was analyzed with the following results, 100 cc. of gas being taken as sample each time.

Analysis I.

100 cc. of gas taken during first and second hours:

	cc.
Carbon dioxide	24.6
Oxygen	9.6
Carbon monoxide	14.6
Nitrogen	51.2

Analysis II.

100 cc. of gas taken during third and fourth hours:

	cc.
Carbon dioxide	73.2

Analysis III.

100 cc. of gas taken during fourth and fifth hours:

	cc.
Carbon dioxide	59.6
Oxygen	9.4
Carbon monoxide	13.6
Nitrogen	17.4

These gas analyses show that the action of the current had taken effect, either in oxidizing some of the carbon of the pyroracemic acid to carbonic acid, or that it had caused a rupture in the molecule $CH_3CO\ COOH$, splitting off carbon dioxide.

The contents of the porous cup were treated as above, and it was noticed at this juncture, that the distillate possessed the odor of acetic ether.

Experiment 3.—About 29 grams of pyroracemic acid were used; all the other conditions were not noted, the object being to get a better insight into the gases by a more rapid evolution of the same from the experimental cell. They were collected in samples of 100 cc. after the current had acted for several hours.

Analysis I.

	cc.
Carbon dioxide	92.8
Oxygen	3.0
Carbon monoxide	1.0
Nitrogen	3.2

Analysis II.

	cc.
Carbon dioxide	85.0
Oxygen	7.8
Carbon monoxide	2.8
Nitrogen	4.4

The samples for these analyses were collected several hours apart and show conclusively that the action of the current had either caused an oxidation or a breaking-down in the molecule of the pyroracemic acid.

The electrolyte in this experiment possessed the color and odor previously observed.

Experiment 4.—Here the conditions were:

Pyroracemic acid	19.87 grams.
Sodium hydroxide	40 grams.
Alcohol	150 cc.
Water	100 cc.
Temperature	Ordinary.
Time	90 hours.
N. $D._{180}$	1.3 amperes.
Voltage	3–4 volts.

Thus far I had collected the gases escaping from the experimental cell over the same water, and I observed that the latter possessed an odor characteristic of aldehyde. The electrolyte, also, if noticed carefully, was found to bear an aldehydic odor, besides that of acetic ether and alcohol.

As a consequence of these observations, an Erlenmeyer flask containing ether was inserted into the exit tube leading to the vessel in which the water was contained, and allowed to remain for several hours, after which the flask was removed and dry ammonia gas passed through the ether. A white precipitate of aldehyde ammonia was the result.

Experiment 5.—The amounts of material varied but little from those in the preceding experiments.

Pyroracemic acid	10 grams.
Sodium hydroxide	10 grams.
Alcohol	100 cc.
Water	85 cc.
Temperature	30°–80° C.
Time	8 hours.
N.$D._{100}$	2.5 amperes.
Voltage	6–20 volts.

With the anode liquid made up as above indicated, the experiment was started and allowed to continue until it became almost a non-conductor, as observed in some of the preceding experiments. The temperature and voltage increased while the amperage naturally decreased.

The gases were passed through ether, as before, and the aldehyde precipitated by ammonia. The yield in this experiment was equal to 0.9656 gram aldehyde, or 19 per cent. of the theoretical.

Here it might be the proper place to offer some theoretical explanation of the reactions so far observed.

First, it seems that aldehyde is the first product of the oxidation, and it appears to be formed by the breaking-down of the acid molecule in this manner:

$$CH_3COCOOH = CH_3CHO + CO_2.$$

Secondly, from the very characteristic odor of acetic ether, which is, without a doubt, present, I conclude that it must be formed from the acetic acid, which would naturally be the next product of the oxidation, and the alcohol present in the solution thus:

$$CH_3CHO + O = CH_3COOH,$$

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O.$$

The singular fact about this is that these reactions took place in a solution that was strongly alkaline to begin with. But as we know that such ethers are generally formed in acid solutions, the pr sence of acetic ether here gives very reliable evidence of the formation of acetic acid as a second product.

Thirdly, another reaction, in all probability, takes place thus:

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH.$$

By this reaction sodium acetate would be formed, regenerating the alcohol.

All these reactions, of course, are only of theoretical interest.

Experiment 6.—The material used was:

Pyroracemic acid	10 grams.
Sodium hydroxide	10 grams.
Alcohol	100 cc.
Water	110 cc.
Temperature	60°–80° C.
Time	5 hours.
$N. D._{100}$	2.5 amperes.
Voltage	6–56 volts.

The cell containing this solution was placed upon a water-bath and was attached to a return condenser, which served to condense any vaporized alcohol. A low flame was applied to keep the temperature within the limits given. A long glass tube connected the

top of the condenser with two Erlenmeyer flasks, which contained anhydrous ether. This tube served to conduct the exuding gases through the ether.

The experiment was interrupted when the bubbles passed slowly through the ether and in place of the return condenser an ordinary Liebig condenser was attached to the anode chamber and the experiment continued. A liquid very like acetic ether in odor began to distil over at 76°-77° C., but almost immediately the temperature rose to 78° C., when alcohol came over. The distillate was collected for several minutes and it had all the appearance and odor of those residual liquids obtained from the ether extractions in the previous experiments.

The change in color of the anode liquid was undoubtedly due to the usual effect of an alkali on aldehyde.

The precipitated aldehyde ammonia in this case equaled 0.7980 gram, equivalent to 0.5755 gram of aldehyde, or one-tenth of the theoretical yield.

The anode liquid was evaporated on the water-bath after filtration, when it gave a tarry residue, from which nothing could be sublimed.

Experiment 7.—The same conditions were observed as given above for Experiment 6, with the exception of the time, which was cut down to four hours and twenty minutes. In this experiment the ether was chilled by ice-water and a copious precipitate of aldehyde ammonia was obtained. It was not weighed.

Experiment 8.—This was performed according to the conditions under Experiment 6. A better yield of aldehyde was obtained. The aldehyde ammonia equaled 4.88 grams, equivalent to 3.41 grams of aldehyde, or about three-fifths of the theoretical.

Experiment 9.—This experiment was performed with the following conditions:

Pyroracemic acid	10 grams.
Sodium hydroxide	10 grams.
Water	110 cc.
Alcohol	100 cc.
Time	$7\frac{1}{2}$ hours.
Temperature	50° C.
N. $D._{100}$	1.35–0.85 amperes.
Voltage	5–40 volts.

Lead electrodes were used. It is seen, from the above data re-

garding amperage and voltage, that the action proceeded along the same line as it does with the platinum electrodes. The aldehyde was precipitated as aldehyde ammonia, as before; it equaled 1.5522 grams. It was thought that the lead peroxide being formed at the anode might aid in the oxidation, but it seems to have no action.

Experiment 10.—The conditions observed here were similar to those of Experiment 9, with the exception of the temperature, which was raised to 70° C. For the platinum electrodes, two carbon electrodes of 45 sq. cm. were substituted. This experiment yielded aldehyde upon the usual treatment. It was not weighed.

It was thought that possibly the carbon would produce milder oxidation, by uniting with the oxygen to form an atmosphere of carbon dioxide, and thus retard the oxidation. In this manner it was hoped to form acetyl superoxide, and then have this break down into diacetyl, thus:

1. $\begin{matrix}CH_3COCOOH\\ \\ CH_3COCOOH\end{matrix} + OOO = H_2O + 2\overline{CO_2} + \begin{matrix}CH_3COO\\ |\\ CH_3COO\end{matrix}$

2. $\begin{matrix}CH_3COO\\ |\\ CH_3COO\end{matrix} + OO = \begin{matrix}CH_3CO\\ |\\ CH_3CO\end{matrix} + 2\overline{O_2}$

As Schall in 1871 claimed to have obtained a persulphide of an analogous formula to that given to acetyl superoxide, it seems, reasoning by analogy, that if diacetyl exists at all it should be obtained from pyroracemic acid, if any acid is to yield it, according to the above indicated reactions.

B. Oxidation in Sulphuric Acid Solution.

Experiment 1.—The following material was employed:

Pyroracemic acid	10 grams.
Sulphuric acid (conc.)	20 cc.
Alcohol	100 cc.
Temperature	60°–80° C.
Time	4½ hours.
N. $D._{100}$	2.5 amperes.
Voltage	3 volts.

This experiment was conducted in an apparatus similar to that employed in the sodium hydroxide solutions. Aldehyde ammonia

was precipitated in the usual manner. The anode liquid had the odor of acetic ether.

Experiment 2.—In this experiment conditions similar to those in Experiment 1 were observed. The anode liquid was shaken out with ether and distilled as usual; the resulting distillate was of the same nature as those produced by the experiments made in sodium hydroxide solution. This is a further proof of the production of acetic acid, as here we have the production of acetic ether in acid solution.

Experiment 3.—The following conditions were observed:

Pyroracemic acid	10 grams.
Alcohol	100 cc.
Sulphuric acid (conc.)	25 cc.
Temperature	50° C.
Time	27 hours.
N. $D._{100}$	0.45 ampere.
Voltage	$2^2/_3$ volts.

The thought entertained here was that with low pressure and density there was a possibility of obtaining diacetyl in sulphuric acid solution. No attempt was made to collect the gases. An inverted condenser was used to return any alcohol. The anode liquor was extracted with ether several times, but nothing new was found.

Experiment 4.—The conditions in this experiment were:

Pyroracemic acid	10 grams.
Sulphuric acid (conc.)	20 cc.
Alcohol	100 cc.
Time	$7^1/_2$ hours.
Temperature	60° C.
N. $D._{100}$	1.4 amperes.
Voltage	$4^1/_2$ volts.

Lead electrodes were employed. Aldehyde was precipitated by ammonia, but was not weighed for the reasons already noted. The anode liquid yielded nothing new.

Experiment 5.—The conditions observed here are similar to those under Experiment 4, with the exception of time and density. The time was three hours and N. $D._{100} = 0.9$ ampere. Carbon electrodes were used. Aldehyde and the other products were obtained. This experiment was interrupted at the point when it

was supposed that the aldehyde would begin to come off, but such a point was not found.

C. *Oxidation in Hydrochloric Acid Solution.*

Experiment 1.—The following conditions were observed:

Pyroracemic acid	10 grams.
Hydrochloric acid (conc.)	30 cc.
Alcohol	100 cc.
Time	5 hours.
Temperature	60°–70° C.
N. $D._{100}$	2.5 amperes.
Voltage	5 volts.

A carbon plate was substituted for the platinum anode in these experiments, otherwise they were conducted as those which precede them. Upon the passage of ammonia gas into the chilled ether a white coloration was produced, but it disappeared after a short time. This was probably due to a little volatilized hydrochloric acid gas in the ether, or perhaps there was sufficient water in the ether to dissolve it. The anode liquid was treated as above, but gave nothing other than what had been noted previously.

Experiment 2.—Here I used:

Pyroracemic acid	20 grams.
Hydrochloric acid (conc.)	60 cc.
Alcohol	150 cc.
Time	24 hours.
Temperature	50° C.
N. $D._{100}$	0.4 ampere.
Voltage	18 volts.

The anode in this experiment was a common graphite pencil with the wood removed at both ends. My hope was that I might obtain diacetyl, but without avail.

Experiment 3.—Material slightly varied again:

Pyroracemic acid	20 grams.
Alcohol	100 cc.
Hydrochloric acid (conc.)	30 cc.
Temperature	40° C.
Time	10 hours.
N. $D._{100}$	1.35 amperes.
Voltage	5 volts

A carbon plate was used. The anode liquid, analyzed as before, revealed nothing new.

D. Oxidation of Certain Salts of Pyroracemic Acid.

The magnesium, sodium and iron salts were made with care and their solutions electrolyzed with the hope of obtaining diacetyl, but it was not found.

E. Oxidation in Sodium Carbonate Solution.

Experiment 1.—Here I used the following:

Pyroracemic acid	10 grams.
Time	6 hours.
Temperature	30° C.
N. $D._{100}$	1.35 amperes.
Voltage	6 volts.

The pyroracemic acid was dissolved in 100 cc. of water and neutralized with sodium carbonate. The cathode liquid was also a solution of sodium carbonate.

It was found that after a time the anode liquid became acid. The escaping gases were tested for carbon dioxide and found to contain 93 per cent. This indicates action similar to that produced in a sodium hydroxide solution.

Experiment 2.—Observing that no diacetyl had as yet been obtained, it was suggested to keep the anode liquid perfectly alkaline by means of sodium carbonate added from time to time; also to keep the cathode liquid as nearly neutral as possible by running a stream of carbon dioxide into the same. With these precautions all of the following experiments were directed to the formation of diacetyl.

Pyroracemic acid	20 grams.
Time	$9\frac{1}{2}$ hours.
Temperature	30° C.
N. $D._{100}$	1.35 amperes.
Voltage	6 volts.

The pyroracemic acid was dissolved in 100 cc. of water and neutralized with sodium carbonate. A small addition of the same was made every half hour. The anode liquid was taken out and distilled over a free flame. The distillate was salted out with common salt and redistilled. This procedure gave a greenish yellow distillate, with a color very like that of diacetyl. This was dehydrated over calcium chloride and distilled again. It retained the same color, but the odor was like that of a weak solution of the pyroracemic acid itself, after being boiled.

The boiling-point of diacetyl (87°-88° C.) was never approached in the distillation of this substance.

Experiment 3.—Again I employed the following:

Pyroracemic acid	20 grams.
Water	100 cc.
Time	10 hours.
Temperature	30° C.
N. $D._{100}$	1.8 amperes.
Voltage	10 volts.

The anode liquor was acidulated with dilute sulphuric acid and then distilled; the distillate was salted out as before and redistilled. It gave a greenish yellow distillate, which was treated according to the method of Pechmann.[1] In accordance with this, normal potassium hydroxide was added to the solution to alkaline reaction, but it did not become colorless or a faint brown as Pechmann asserts. It, however, became a light yellow in color. It was then acidulated with dilute sulphuric acid and extracted several times with ether. The ether was distilled off and a yellowish green substance was left instead of a colorless oil as directed.

The object of this treatment was to form if possible the aldol of diacetyl.

From what I obtained from the ether extractions, I attempted to produce *p*-xyloquinone, by treatment with potassium hydroxide, which would constitute a conclusive test for diacetyl. This, however, was not obtained. The *p*-xyloquinone is described as a golden yellow crystalline compound, crystallizing from alcohol in needles and subliming undecomposed. No product of such characteristics appeared in the attempted transformations.

Still laboring under the impression that possibly that greenish yellow material might be the sought-for substance, several experiments were tried, some with the same conditions as those given above and others with conditions slightly different. The anode liquids were all treated as has been described, but no test for diacetyl revealed its presence.

EXPERIMENTAL, PART II.

In the reduction of pyroracemic acid the porous cup was made the cathode chamber.

[1] *Ber. d. chem. Ges.*, **28**, 1846.

A. Reduction in Sodium Hydroxide Solution.

Experiment 1.—The following material was employed:

Pyroracemic acid	5 grams.
Alcohol	50 cc.
Water	50 cc.
Sodium hydroxide	8 grams.
Temperature	Ordinary.
Time	7 hours.
N. $D._{100}$	0.45 ampere.
Voltage	$3^1/_2$ volts.

The lactic acid in the cathode liquid was estimated according to the directions in Beilstein's "Handbook" as follows: It was acidulated with dilute sulphuric acid and extracted with ether several times. The ether was evaporated and the residual liquid heated in a porcelain dish for some minutes on a water-bath to expel any dissolved ether. Lead acetate was added to remove any sulphuric acid present. The lead sulphate formed was filtered off and more lead acetate added together with alcoholic ammonia (alcohol 90 per cent., ammonia 10 per cent.) until no further precipitation was noticed. A white, slimy precipitate was obtained, which, according to Beilstein, has the composition, $3PbO.C_3H_6O_3$. This was filtered off, washed with alcohol, dried at 100° C., and weighed. The same writer mentions that this precipitate contains 78.5 per cent. lead oxide; therefore there is 21.5 per cent. free lactic acid contained in it. The precipitate in this case weighed 2.595 grams, corresponding to 0.5579 gram of lactic acid.

According to the equation

$$CH_3COCOOH + H_2 = CH_3CH(OH)COOH,$$

10.91 per cent. of the theoretical yield was obtained.

Experiment 2.—Here I used:

Pyroracemic acid	5 grams.
Alcohol	75 cc.
Water	50 cc.
Sodium hydroxide	10 grams.
Temperature	Ordinary.
Time	5 hours.
N. $D._{100}$	0.8 ampere.
Voltage	4 volts.

The cathode liquid was acidulated and treated as above. The precipitate weighed 6.7581 grams, equivalent to 1.4529 grams of lactic acid, or 28.43 per cent. of the theory.

Experiment 3.—The material was:

Pyroracemic acid	5 grams.
Sodium hydroxide	8 grams.
Alcohol	50 cc.
Water	50 cc.
Temperature	50° C.
Time	6 hours.
N. $D._{100}$	0.7 ampere.
Voltage	4 volts.

The cathode liquid under the prescribed treatment yielded 3.9592 grams of precipitate, corresponding to 0.8512 gram lactic acid, equivalent to 16.65 per cent. of theory.

In the preceding experiments platinum electrodes were employed.

Experiment 4.—Lead electrodes were used in this experiment with conditions as follows:

Pyroracemic acid	20 grams.
Sodium hydroxide	10 grams.
Alcohol	100 cc.
Water	110 cc.
Temperature	60° C.
Time	5 hours.
N. $D._{100}$	0.9 ampere.
Voltage	5–6 volts.

The cathode liquid, treated as usual, gave 4.5860 grams of the lead salt, corresponding to 0.9859 gram of lactic acid, equivalent to 9.64 per cent. of theory.

B. Reduction in Sulphuric Acid Solution.

Experiment 1.—Here I used:

Pyroracemic acid	10 grams.
Alcohol	75 cc.
Sulphuric acid (conc.)	20 cc.
Temperature	30° C.
Time	21 hours.
N. $D._{100}$	0.45 ampere.
Voltage	3 volts.

The cathode liquid was directly shaken out with ether, as it was an acid solution, otherwise treatment was the same as when working in an alkaline solution. It yielded 3.0499 grams of the lead salt, corresponding to 0.6557 gram of lactic acid, equivalent to 6.41 per cent. of the theory.

Experiment 2.—The following was used:

Pyroracemic acid	10 grams.
Sulphuric acid (conc.)	20 cc.
Alcohol	75 cc.
Temperature	30° C.
Time	9 hours.
N. $D._{100}$	0.45 ampere.
Voltage	3 volts.

The cathode liquid gave 7.1718 grams of the lead salt, corresponding to 1.5417 grams of lactic acid, equivalent to 15.08 per cent. of the theory.

Experiment 3.—Here I used:

Pyroracemic acid	5 grams.
Sulphuric acid (conc.)	20 cc.
Alcohol	75 cc.
Temperature	30° C.
Time	6 hours.
N. $D._{100}$	0.6 ampere.
Voltage	$3^1/_2$ volts.

The usual treatment gave 5.3731 grams of the lead salt, corresponding to 1.1552 grams of lactic acid, equivalent to 22.60 per cent. of the theory.

Experiment 4.—Here the following were used:

Pyroracemic acid	5 grams.
Water	50 cc.
Sulphuric acid (conc.)	25 cc.
Alcohol	50 cc.
Time	6 hours.
Temperature	35° C.
N. $D._{100}$	0.8 ampere.
Voltage	$3^1/_2$ volts.

This yielded 6.4670 grams of the lead salt, corresponding to 1.3904 grams of lactic acid, equivalent to 27.19 per cent. of the theory. Platinum electrodes were used in these experiments.

Experiment 5.—Lead electrodes were used in this experiment with the following conditions:

Pyroracemic acid	10 grams.
Sulphuric acid (conc.)	10 cc.
Alcohol	100 cc.
Temperature	50° C.
Time	$4^1/_2$ hours.
N. $D._{100}$	0.85 ampere.
Voltage	5–6 volts.

The yield was 3.3203 grams of the lead salt, corresponding to 0.7138 gram of lactic acid, equivalent to 6.97 per cent. of the theory.

Experiment 6.—Carbon electrodes were employed here with the following conditions:

Pyroracemic acid	10 grams.
Sulphuric acid (conc.)	15 cc.
Alcohol	100 cc.
Water	50 cc.
Temperature	60° C.
Time	$4^1/_2$ hours.
N. $D._{45}$	0.9 ampere.
Voltage	3.5 volts.

The cathode liquid gave 3.7693 grams of the lead salt, corresponding to 0.8103 gram of lactic acid, equivalent to 7.93 per cent. of the theory.

It might be well to state the maximum and minimum yields of lactic acid.

In alkaline solution under the conditions of experiment (2) the maximum was obtained, under those of (4), the minimum. The figures are 28.43 and 9.64 per cent. of the theoretical yields.

In sulphuric acid solution, under experiment (4), the maximum 27.19 per cent., and under experiment (1), the minimum, 6.41 per cent., of the theoretical was obtained.

In the reduction of pyroracemic acid by electrolytic hydrogen, it seems natural that lactic acid should be the first product of the reduction; also, that by further reduction propionic acid should be obtained.

The latter, in my opinion, is formed at least in small quantities and probably, if exceedingly large quantities of pyroracemic acid were electrolyzed and treated as described, it would be found.

Further, it is noticed in this part also, that the change in the kind of electrodes causes no marked difference.

As a final conclusion it may be stated that this study reveals as products of the electrolytic oxidation and reduction of pyroracemic acid—acetaldehyde, acetic acid, acetic ester, and lactic acid with some probability of diacetyl and propionic acid.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTIONS FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE SIGNIFICANCE OF PHOSPHATES IN NATURAL WATERS.

BY A. G. WOODMAN.

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THE determination of phosphates in a drinking-water is a matter which has not received the attention from water analysts that has been given to the estimation of various other constituents. Any one who looks through the literature cannot help noticing how few are the published results of quantitative estimations of the phosphate content of natural waters, apart from mineral waters. Yet this determination, by reason of the conversion of organic phosphorus compounds into phosphates through the processes of decay, is one which might reasonably be expected to throw considerable light on the question of the pollution of natural waters by objectionable material.

The reasons for this dearth ot published data are not far to seek. To be of value the amount of phosphate must be known within rather narrow limits. Qualitative tests are not sufficient. The mere presence of phosphates is by no means definite or even confirmatory evidence of organic pollution. Rocks and minerals containing phosphates are found nearly everywhere and traces, at times even considerable quantities, may be dissolved, especially by waters rich in carbonic acid. This, however, does not constitute a serious objection to the utility of the determination. The same is true of many, if not most, of the constituents upon which reliance is placed in judging of the quality of a water. Unpolluted waters often contain notable amounts of nitrates and chlorides and a true judgment can be rendered only after comparison with samples from adjacent but unpolluted sources.

The chief reason, however, has been the lack of an accurate and simple method, sufficiently delicate, and of enough data to work out a standard for comparison. It is even declared, with some authority, that the determination is entirely worthless. Wanklyn says of it:[1] "Much nonsense has been talked about phosphates in drinking-water; and the fact has been overlooked that, except as

[1] "Water Analysis," p. 109 (1891).

infinitesimal traces, they cannot exist along with carbonate of lime in a clear water." And at a later date Thresh remarks:[1] "The difficulty of detecting phosphates, when silica is also present, as is usually the case, the still greater difficulty of estimating the quantity, and the very doubtful value of the information when obtained, has caused most chemists to ignore their presence. Traces may be found in wholesome waters, and their absence affords no proof that a water is free from pollution, hence the determination is useless."

That, in spite of Wanklyn's statement to the contrary, appreciable quantities of phosphates may exist in natural waters along with carbonate of lime, has been shown by Hehner.[2] It is pointed out that, theoretically, from the established solubility of calcium phosphate a water may contain 36.6 parts of phosphorus pentoxide per million; and that water saturated with carbon dioxide, a condition which frequently does exist, may hold in solution as much as 67.5 parts of phosphorus pentoxide in a million, which is quite as large an amount as is the case with several of the mineral constituents usually determined. In an actual case cited the amount of phosphate found was 5.5 parts phosphorus pentoxide per million, and Harvey[3] found 14.7 parts in a well water from the chalk formation.

The second objection, the lack of a simple and accurate process of estimation, is no longer valid since the former gravimetric methods, which were tedious and introduced the liability to serious error in concentrating large volumes of water, have been replaced by colorimetric methods. The colorimetric processes, which are based in general upon the reaction with alkali molybdates, as proposed in 1880 by J. West-Knights[4] and later improved by Lepierre[5] and by Jolles and Neurath,[6] have been critically studied in this laboratory[7] and the method finally adopted seems to solve the problem in a satisfactory manner. The method as applied to colorless waters, for which it is best suited, may, for convenience, be briefly repeated here.

[1] "Water Supplies," p. 170 (1896).
[2] *Analyst*, 5, 135 (1880).
[3] *Ibid.*, p. 197.
[4] *Ibid.*, 5, 197 (1880).
[5] *Bull. Soc. Chim.*, 15, 1213 (1896).
[6] *Monatsh. Chem.*, 19, 5 (1898).
[7] Woodman and Cayvan: This Journal, 23, 96 (1901).

Fifty cc. of the water and 3 cc. of nitric acid (sp. gr. 1.07) are evaporated to dryness in a 3-inch porcelain dish on a water-bath. The residue is heated in an oven for two hours at the temperature of boiling water. The dry residue is then treated with 50 cc. of cold distilled water, added in several portions, and poured into the comparison tube. It is not necessary to filter the solution. Four cc. of ammonium molybdate (50 grams per liter) and 2 cc. of nitric acid are added, the contents of the tube mixed, and the color compared, after three minutes, with standards made by diluting varying quantities of the standard phosphate solution (1 cc. = 0.0001 gram phosphorus pentoxide) to 50 cc., and adding the reagents as above. A blank should always be made on the distilled water used for dilution, especially if it has stood for any length of time in glass vessels.

The method as outlined has been used on a number of waters from various sources which have been examined from time to time and the results, together with the figures for the other important determinations usually made are given in the accompanying tables. For convenience they are divided roughly into three classes: waters which may fairly be considered unpolluted; samples of doubtful purity; waters plainly polluted. This classification is based on the amounts of the other constituents rather than on the quantity of phosphate in order to determine the valuation and limits of the latter. Table IV gives the results of analysis of several samples from the same general source, showing the correspondence of the various constituents under varying conditions. The results are given in all cases in parts per million.

On examining the results it will be observed that the amount of phosphate shows considerable variations for a given class of waters, which might indeed well be expected when we take into consideration the readiness with which it is absorbed or precipitated. It has been found too, that it seems to be more or less dependent upon the amount of iron, an instance of which will be found in No. 20 of Table III; a part of the phosphate has been removed, no doubt, by sedimentation as ferric phosphate.

In Table I samples 2 and 3 had been standing in the collecting bottles for some time before being analyzed, which would have a tendency to make the results too high. Sample 9 is interesting by comparison with a sample from the same source (III, 8) taken

TABLE I.—UNPOLLUTED WATERS.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Southboro, Mass		0.008	0.060	0.000	0.000	1.8	11.1	0.90	Spring in the woods.
2	Newburyport, Mass....	50.0	0.002	0.024	0.001	0.400	9.2		2.7	City supply—driven wells.
3	Belmont, Mass		0.006	0.008	0.001	0.500	3.29		1.7	Spring.
4	Lowell, Mass.....	102.0	0.012	0.046	0.000	0.400	2.7		0.54	City supply.
5	Winsted, Conn.....	31.5	0.017	0.020	0.000	0.000	4.2		0.44	Spring—no contamination.
6	Poughkeepsie, N. Y...		0.003	0.010	0.002	1.250	5.8		0.4	Purified water.
7	Dublin, N. H.....		0.006	0.016	0.000	0.000	1.6	8.0	0.08	
8	Dublin, N. H.....		0.008	0.006	0.000	0.080	0.8	9.0	0.14	
9	Jamaica Pond, Mass...		0.014	0.406	0.000	0.000	8.0		0.20	Heavy growth of organisms —*Oscillatoria prolifica*.
10	Marion, Mass		0.004	0.120	0.000	0.600	94.0		0.70	Near salt water.
11	Marion, Mass		0.002	0.002	0.008	0.400	11.2	30.9	0.80	Artesian well.
12	Marion, Mass		0.000	0.024	0.000	0.150	12.0	55.0	0.14	Milky with clay.
13	Bedford, Mass		0.002	0.008	0.000	0.100	3.0	38.0	0.80	
14	Essex, Mass		0.018	0.070	0.001	0.350	7.0	21.0	0.0	Cistern, unpolluted.
15	Essex, Mass	85.0		0.096		0.560	10.5		0.54	Spring near tide-water.

TABLE II.—DOUBTFUL WATERS.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Canton, Mass		0.002	0.032		1.600	40.0		0.4	
2	Canton, Mass.....	61.0	0.005	0.024	0.000	1.600	7.2		1.6	
3	Winsted, Conn.....	200.0	0.240	0.070	0.019	4.900	25.4		0.26	
4	Cambridge, Mass.....	116.0	0.004	0.032	0.000	3.000	8.24		1.8	
5	Essex, Mass.....	214.0	0.000	0.052	0.002	4.500	16.0	...	3.0	Pump and watering trough near road.
6	Canaan, N. H.....		0.086	0.154	0.015	2.500	4.0		1.6	
7	Canaan, N. H.....		0.012	0.068	0.000	2.000	4.0		1.6	
8	Bedford, Mass.....	72.5	0.000	0.012	0.003	1.100	4.4	26.0	0.80	Milky with clay.
9	Jamaica Plain, Mass....	109.5	0.032	0.002	0.000	2.000	12.0	47.0	0.60	On hill—few houses near.
10	Boxford, Mass.....		0.000	0.032	0.000	0.900	6.0	61.0	1.2	Well near road.
11	Boxford, Mass.....		0.000	0.024	0.000	1.900	2.5	20.0	1.8	Well at foot of hill.
12	Hopkinton, Mass.....	. ..	0.004	0.000	0.000	0.450	4.8		2.2	
13	Essex, Mass.....		0.014	0.092	0.000	0.560		41.6	1.4	Well in pasture.
14	Mattapoisett, Mass.....		0.004	0.026	0.016	1.850	19.0	41.6	0.4	
15	Wenham, Mass.....	188.0	0.008	0.106	0.030	0.500	10.8		1.7	

TABLE III.—POLLUTED WATERS.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Newburyport, Mass...	322.5	0.026	0.090	0.008	42.5	57.1		3.6	
2	Beverly, Mass.....	227.0		0.028	0.001	16.000	20.1		3.8	
3	Everett, Mass.....		0.008	0.018	0.004	19.000	26.1		6.8	Spring water sold in city.
4	Essex, Mass.....		0.010	0.050	0.010	10.000	36.7		8.6	Town pump.
5	Framingham, Mass...	691.0	0.930	0.080	0.010	50.000	72.2		3.8	Well in barnyard.
6	Newburyport, Mass...	88.0	0.010	0.016	0.000	7.000	20.4		1.8	Driven well.
7	Canton, Mass.....	...	0.000	0.034	0.000	11.000	46.1		3.8	
8	Jamaica Pond, Mass...	67.5	0.010	0.134	0.003	0.220	8.4		3.7	Pond practically free from *Oscillatoria*.
9	Essex, Mass	200.0	0.000	0.036	0.000	2.250	32.5		8.0	Well near the house.
10	Poughkeepsie, N. Y...	20.6	0.013	0.150	0.006	1.750	5.2		1.4	Brook contaminated by sewage effluent.
11	Poughkeepsie, N. Y...	21.3	0.029	0.140	0.011	0.600	11.3		3.8	Brook contaminated by sewage effluent.
12	Poughkeepsie, N. Y...		0.004	0.046	0.010	6.500	25.1		9.0	Brook contaminated by sewage effluent.
13	Bedford, Mass.....	203.0	0.004	0.108	0.000	5.500	6.7	57.0	1.4	
14	Canaan, N. H.....		0.006	0.112	0.002	15.000	32.0	110.0	4.0	
15	Long Island, N. Y....	836.0	0.006	0.036	0.003	34.000	80.0	400.0	3.2	Artesian well.
16	Newport, R. I.....	142.0	0.008	0.026	0.001	3.750	16.0	46.0	2.0	
17	Annisquam, Mass....		0.014	0.006	0.000	2.250	35.0	38.0	2.4	
18	W. Falmouth, Mass...		0.084	0.100	0.010	4.500	38.0	43.0	2.4	
19	Essex, Mass.....		0.014	0.054	0.002	8.330	41.0	104.5	13.3	Well—large henyard on slope above.
20	Natick, Mass.....		0.120	0.080	0.022	16.600	47.8		2.6	Sewage effluent—high in iron.

TABLE III.—POLLUTED WATERS (*Continued*).

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
21	Malden, Mass.....		0.000	0.016	0.002	7.500	60.8	81.4	7.4	Well surrounded by drains and cesspools.
22	Canton, Mass.....	113.0	0.000	0.038	0.000	3.500	23.5	36.2	5.0	Used only for garden.
23	Newport, R. I.....		0.248	0.068	0.500	8.500	83.0	121.1	4.6	Typhoid fever among families using this well.
24	Marblehead, Mass....	360.0	0.000	0.080	0.018	7.500	47.0	140.4	5.6	Surrounded by houses.
25	Marblehead, Mass...	609.0	0.000	0.080	0.008	19.000	56.0	264.5	6.8	Surrounded by houses.
26	Thompson, Conn.....		0.000	0.008	0.000	1.850	4.04	42.9	6.6	
27	Thompson, Conn....	...	0.042	0.046	0.000	2.450	1.04	20.8	3.6	
28	Essex, Mass.....	235.0	0.008	0.040	0.000	3.500	46.6	74.3	4.7	
29	Essex, Mass.....	520.0	0.016	0.088	0 001	5.250	90.6	205.6	7.6	Sink drain within 4 feet of well.
30	Boxford, Mass.....		0.002	0.032	0.000	20.000	24.1	132.0	4.8	Well about 50 feet from barn.
31	Dartmouth, Mass.....		0.000	0.008	0.000	2.850	8.2	27.3	3.3	
32	Hopkinton, Mass.....		0.006	0.004	0.008	7.000	5.9		5.4	
33	So. Essex, Mass.....	409.0	0.050	0.078	0.007	7.500	93.8	151.4	4.2	Well between house and barn.
34	So. Essex, Mass.....	290.0	0.116	0.130	0.004	11.200	37.3	180.2	4.9	Well in yard near house.
35	Essex, Mass.....		0.000	0.012	0.000	3.050	40.6	60.0	6.0	Spring on slope from cemetery.
36	W. Falmouth, Mass..	169.0	0.000	0.026	0.000	4.500	39.0	45.7	4.0	
37	Stoneham, Mass.....		0.082	0.028	0.001	24.000	14.0	125.6	3.2	Spring, cesspool found beside it.
38	Southboro, Mass.....	124.0	0.000	0.000	0.000	3.000	10.0		4.0	Well in pasture.
39	Jamaica Plain, Mass..		0.010	0.030	0.001	4.250	30.8	114.3	6.6	Well in cellar of house.
40	Jamaica Plain, Mass..		0.000	0.028	0.000	4.000	19.2	70.7	4.9	21 feet deep, near house.
41	Jamaica Plain, Mass..		0.010	0.024	0.000	4.000	20.2	71.3	4.6	108 feet deep, in barnyard.
42	Cambridge, Mass.....		0.034	0.028	0.160	19.000	17.5	126.0	1.3	

TABLE IV.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Sayre, Pa	266.0	0.001	0.018	0.001	1.500	9.7	183.4	2.9	Supply well after pumping out six times.
2	Sayre, Pa	293.0	0.000	0.000	0.000	1.600	12.4	196.6	3.1	Pump in driven well back of station.
3	Sayre, Pa	121.0	0.018	0.042	0.000	0.120	5.0	79.4	0.70	River at "intake."
4	Sayre, Pa	257.0	0.000	0.006	0.001	1.500	9.8	182.8	3.1	Supply well after pumping out nine times.
5	Sayre, Pa	106.0	0.005	0.058	0.000	0.070	4.4	76.8	0.70	House faucet from tap in town.
6	Sayre, Pa	258.0	0.000	0.022	0.001	1.440	9.7	182.8	3.1	Supply well after pumping out three times.

under different conditions, as showing the change in phosphate content through the increase of organic life.

The amount of phosphate and its variation seem to follow the same general line as the other mineral constituents which either accompany the polluting material or are produced by its decay, especially the nitrates and chlorides. It is not, however, so delicate an indicator as these. This correspondence is well shown in the samples in Table IV and also in samples 10 to 12 of Table III, where the increased pollution, as evidenced by the gradual increase in chlorine, is accompanied by increased phosphate.

The results obtained by the colorimetric method would seem to indicate that the limit of 0.5 part of phosphorus pentoxide in a million, as given by Hehner for unpolluted waters, is rather low. A safer amount would be 1.0 part, although the average would doubtless be lower than this.

The highest amount found was 13.3 parts, in sample 19 of Table III. The same rather surprising cases were found as noticed by Hehner in which the amount of phosphate is very much lower than would be expected from the source of the water and the other constituents determined, which may be due to the character of the soil through which the water has percolated. Even with all the drawbacks which are noted there can be no question, in view of the figures given above, that the presence of phosphates in a water in any quantity is significant of pollution, and the determination must be considered as another link (of which we have none too many, anyway) in the chain of circumstantial evidence by which we are often compelled to judge the purity of a water.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS., March, 1902.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(FIFTH PAPER.)

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

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IN this paper we describe a number of exceptions to the rule that the only halogen compounds which undergo any material

conversion into isothiocyanate, by acting on potassium thiocyanate in benzene or alcoholic solutions, are those in which the halogen is in direct combination with a negative group, as in the case of the acyl halides.[1] This rule, until recently, was supposed to be general for all except the allyl halides. The formation of isothiocyanates by the latter had already been ascribed to the negative character of the allyl group.[2]

The view that a strong negative character favors the formation of isothiocyanates appears to be supported by the fact that 2,4-dinitrochlorbenzene gives a normal thiocyanate, $C_6H_3(NO_2)_2SCN$, while 2,4,6-trinitrobenzene gives an isothiocyanate, $C_6H_2(NO_2)_3NCS$.[3]

In the first paper[4] of this series it was shown that certain more or less negative halogen compounds, which were supposed to give isothiocyanates, in reality give nothing but normal thiocyanates. In the second[5] the combined influence of several negative groups together was considered, and it was found that when two hydrogen atoms in methyl bromide were replaced by two phenyl groups another exception to the above rule resulted. Diphenylmethyl bromide was found to give an isothiocyanate. The presence of three phenyl groups, on the other hand, and also of one, two, or three carboxyl groups, did not confer on the substituted methyl halide the property of forming isothiocyanate.

The third paper[6] dealt with dirhodanides, but no isothiocyanates, were observed in these cases.

In the fourth[7] a series of tertiary halides were examined and here again no exceptions to the above rule were found.

From these results, especially those in the second paper, it would seem that the tendency to form isothiocyanate is not dependent on, or proportional to, the negative character of the halide, for it would seem probable that triphenylmethyl bromide is a more negative halide than diphenylmethyl bromide, and di- and tricarbethoxymethyl bromide more negative than the latter. This, as already pointed out, is indicated by comparing the affinity-

[1] Dixon: *J. Chem. Soc.* (London), **75**, 390 (1899).
[2] Michael: *J. prakt. Chem.*, **37**, 509 (1888).
[3] Crocker: *J. Chem. Soc.* (London), **81**, 436 (1902).
[4] This Journal, **23**, 283 (1901).
[5] *Am. Chem. J.*, **26**, 345 (1901).
[6] This Journal, **24**, 439.
[7] *Ibid.*, **24**, 680.

constants of acids that contain these groups. It must be remarked, however, that Vorländer,[1] in his interesting paper "Ueber die Natur der Radicale," calls attention to the fact that this method of deciding negative character can not be relied upon.

The work done in this laboratory has also shown that of the twenty possible halides which can be formed by substituting the three groups. $-CH_3$, $-C_6H_5$, and $-CO_2C_2H_5$, for hydrogen in methyl bromide, only one of these, namely, diphenylmethyl bromide, gives an isothiocyanate. It appears now that this unique behavior is general in the case of those substituted methyl bromides which contain two aromatic radicals.

We have found that phenyl-α-naphthylmethyl and di-α-naphthylmethyl bromides give isothiocyanates. Phenylparatolylmethyl bromide, $C_6H_5CHBrC_6H_4CH_3$, from the carbinol and hydrogen bromide, also gives an isothiocyanate, while, on the other hand, the isomeric halide, parabenzyl-1′-bromtoluene, $C_6H_5CH_2C_6H_4CH_2Br$, forms a normal thiocyanate.

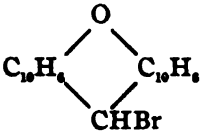
That the rhodanides are isothiocyanates follows from the fact that they react at ordinary temperature with amines yielding thioureas, and also, from their action with thioacetic and thiobenzoic acids, when carbon disulphide is evolved and substituted amides are formed.

The fact that the above bromides react with potassium thiocyanate, and the ease with which the isothiocyanates react with amines (especially β-naphthylamine) to form difficultly soluble ureas, afford an easy test for the position of halogens in the homologues and analogues of diphenylmethane. For example, on brominating *p*-benzyltoluene at 130°-135°, and converting the product into rhodanide, it was easy by means of β-naphthylamine to show that phenylparatolylmethyl bromide had been formed, or in other words, that hydrogen in the CH_2 group had been substituted. According to Senff[2] the corresponding metabenzyltoluene is attacked only in the CH_3 group.

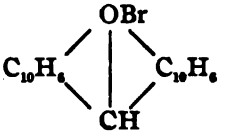
Again, if, as formerly considered, the bromxanthenes, bromdinaphtoxanthene, etc., have the structure represented by Formula I, it might be expected that they would yield isothiocyanates, while

[1] *Ann. Chem.* (Liebig), **320**, 99 (1902).
[2] *Ibid.*, **220**, 240 (1883).

according to the latest representation,[1] II, they probably would not.



I.

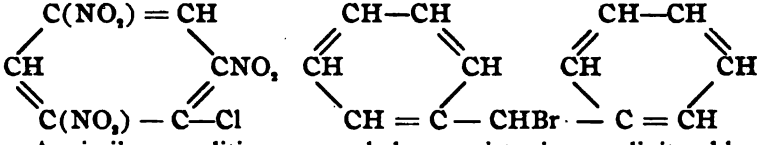


II.

A qualitative test with β-naphthylamine, in fact, after boiling the bromide in chloroform with potassium thiocyanate, failed to give any evidence of the formation of an isothiocyanate.

If the aryl groups are given Kekulé's formula, then the alkyl halides which have thus far been found to give isothiocyanates have one common property. There is either a double bond or at least an unsaturated condition in the 2,3-position:

$$CH_2 = CH - CH_2I,$$



A similar condition, nevertheless, exists in 2,4-dinitrochlorbenzene and in 1'-bromethylbenzene, in brommalonic ester and in the α-halogen acid derivatives, $ClCH_2CO.R$, in general; but none of these halides gives isothiocyanate. This would seem to indicate that a sufficiently negative character as well as an unsaturated condition is required for the formation of isothiocyanates. In how far this idea is applicable and what other influences are at work, cannot be judged from the few data at hand.

EXPERIMENTAL PART.

Phenylparatolylmethylbromide, $C_6H_5CHBrC_6H_4CH_3$.—Phenylparatolyl carbinol was heated to 100° in a stream of dry hydrogen bromide, whereupon water was evolved and the required increase in weight took place. The product, a thin red oil, was then dried in a vacuum at 100° for analysis. A bromine determination gave:

	Calculated for $C_{14}H_{13}Br$.	Found.
Bromine	30.65	30.40

This bromide refused to solidify in a freezing-mixture or on

[1] Werner: *Ber. d. chem. Ges.*, **34**, 3303 (1901); Posse: *Compt. rend.*, **133**, 101 (1901); **134**, 64 (1502).

standing exposed to the air for over three weeks. No attempt was made to distil the oil since diphenylmethyl bromide is decomposed by this treatment even in a vacuum.

Phenylparatolylmethylisothiocyanate, $C_6H_5CH(NCS)C_6H_4CH_3$, was obtained by heating a benzene solution of the bromide with potassium thiocyanate for two days. The product was a thin reddish colored oil, the vapor of which, especially when warmed, had an irritating action on the eyes. A nitrogen determination gave:

	Calculated for $C_{15}H_{13}NS$.	Found.
Nitrogen	5.85	5.72

Phenylparatolylmethylacetamide, $C_6H_5(CH_3C_6H_4)CHNHCOCH_3$.—Two grams of the isothiocyanate, 1.5 grams of thioacetic acid and 2 volumes of benzene were heated somewhat over two hours on the steam-bath. On evaporating the benzene, carbon disulphide was found in quantity, and the residue taken up in ether, washed with alkali and water, gave colorless, flat, rectangular prisms, on evaporating the solvent. This amide is soluble in hot water but on cooling it separates as an oil. For analysis it was crystallized from ether, whereupon it melted at 129.5°-131°, and a nitrogen determination of the sulphur-free material gave:

	Calculated for $C_{16}H_{17}ON$.	Found.
Nitrogen	5.85	6.12

Phenylparatolylmethylthiourea, $C_6H_5(CH_3C_6H_4)CHNHCSNH_2$, was obtained by dissolving the isothiocyanate in alcoholic ammonia. It separated from alcohol in clusters or balls of colorless needles which melted at 162°-163° and gave the following result on analysis:

	Calculated for $C_{15}H_{16}N_2S$.	Found.
Nitrogen	10.93	11.13

Phenylparatolylmethylphenylthiourea, $C_6H_5(CH_3C_6H_4)CHNHCSNHC_6H_5$.—The isothiocyanate reacted immediately with aniline. The product formed colorless, flat prisms from alcohol, which melted at 159°. A nitrogen determination gave:

	Calculated for $C_{21}H_{20}N_2S$.	Found.
Nitrogen	8.4	8.5

Phenylparatolylmethyl-β-naphthylthiourea, $C_6H_5(CH_3C_6H_4)CHNHCSNHC_{10}H_7$, forms as a precipitate when alcoholic solutions of the rhodanide and β-naphthylamine are mixed. It crystallizes from alcohol in bunches of slender, colorless needles melting at 170°. A nitrogen determination gave:

	Calculated for $C_{25}H_{22}N_2S$.	Found.
Nitrogen	7.73	7.70

The Bromination of Parabenzyltoluene.—The hydrocarbon was brominated at 130°-135° and the product was distilled at 11 mm. pressure, whereupon it boiled quite constantly at 179°-180°. It formed a heavy, pale yellow oil. The amount of replaceable bromine was determined by means of sodium ethylate:

	Calculated for $C_{14}H_{13}Br$.	Found.
Bromine	30.65	27.74

The brominated material was heated with potassium thiocyanate in benzene solution for two days. An oil was thus obtained which responded to the reduction test for a normal thiocyanate. A nitrogen determination gave 5.18 per cent. nitrogen instead of 5.85 per cent. An alcoholic solution was allowed to stand with β-naphthylamine, and one with ammonia. In both cases a small amount of crystals was obtained which were identical with the corresponding ureas described above from phenylparatolylisothiocyanate prepared from the carbinol. This shows that on brominating benzyltoluene a portion of the bromine enters the CH_3 group.

Phenyl-α-naphthylmethylbromide, $C_6H_5(C_{10}H_7)CHBr$.—Miquel[1] obtained this bromide by brominating α-benzylnaphthalene, either hot or cold or in carbon disulphide solution. He found that it was a syrup. Our material was prepared by brominating the hydrocarbon at 140°-150°, under the same conditions as the crystalline diphenylmethyl bromide is obtained.[2] The product formed a dark red oil which was dried over potash for analysis. The amount of replaceable bromine was then determined by warming a sample with sodium ethylate:

	Calculated for $C_{17}H_{13}Br$.	Found.
Bromine	26.9	24.6

[1] *Bull. Soc. Chim.* [2], **26**, 4 (1876).

[2] Friedel, Balsohn: *Bull. Soc. Chim.*, **33**, 339.

Phenyl-α-naphthylmethylisothiocyanate,
$C_6H_5(C_{10}H_7)CHNCS$.—A benzene solution of the bromide was heated for forty-eight hours with potassium thiocyanate. On filtering and evaporating the benzene a thick red oil was obtained which deposited nothing solid on cooling. An attempt to purify a portion by distilling under reduced pressure resulted in complete decomposition of the material, some naphthylphenylmethane being obtained. A portion was treated with alcohol and sodium, whereupon it was found that sodium cyanide and thiocyanate were formed. This indicates the presence of normal thiocyanate. The crude oil was dried in a vacuum for analysis and a nitrogen determination then gave:

	Calculated for $C_{18}H_{13}NS$.	Found.
Nitrogen	5.09	4.27

When a portion of this oil was allowed to stand for about six months it solidified. It then formed small plates, from petroleum ether, melting at 76°-77°.

Phenyl-α-naphthylmethylacetamide,
$C_6H_5(C_{10}H_7)CHNHCOCH_3$.—Ten grams of the crude isothiocyanate, in benzene solution, were mixed with 2.8 grams of thioacetic acid and heated upon the steam-bath for three hours. Carbon disulphide was evolved and the acetamide separated on cooling the solution. When crystallized from toluene and some alcohol, small needles were obtained which melted at about 210°. A nitrogen determination gave:

	Calculated for $C_{19}H_{17}ON$.	Found.
Nitrogen	5.09	5.23

Phenyl-α-naphthylmethylbenzamide,
$C_6H_5(C_{10}H_7)CHNHCOC_6H_5$.—Ten grams of the rhodanide were heated for an hour with the calculated amount of thiobenzoic acid. On evaporating the benzene, carbon disulphide was found in quantity by the xanthate test. The benzamide was crystallized from alcohol; it then melted at 158° and a nitrogen determination in the sulphur-free material gave:

	Calculated for $C_{24}H_{19}ON$.	Found.
Nitrogen	4.15	4.11

Phenyl-α naphthylmethylthiourea,
$C_6H_5(C_{10}H_7)CHNHCSNH_2$.—A solution of the isothiocyanate

in alcoholic ammonia was obtained and in a half hour, radiating masses of flat rectangular prisms separated. They were crystallized from alcohol and melted at 197°-198°. A nitrogen determination gave:

	Calculated for $C_{18}H_{16}N_2S$.	Found.
Nitrogen	9.58	9.59

This thiourea is insoluble in water and very difficultly soluble in 20 per cent. sodium hydroxide.

Phenyl-α-naphthylmethylmethylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHCH_3$.—Three grams of the isothiocyanate were dissolved in alcohol and an excess of a 33 per cent. solution of methylamine was added. After standing some time small prisms arranged in clusters separated. They were crystallized from alcohol and melted at 175°-176°. A nitrogen determination gave:

	Calculated for $C_{19}H_{18}N_2S$.	Found.
Nitrogen	9.1	8.8

Phenyl-α-naphthylmethyldiethylthiourea, $C_6H_5(C_{10}H_7)CHNHCSN(C_2H_5)_2$, from the isothiocyanate and diethylamine, formed clusters of flat prisms or a sandy powder. It melted at 112°-113° and a nitrogen determination gave:

	Calculated for $C_{23}H_{26}N_2S$.	Found.
Nitrogen	8.04	8.00

Phenyl-α-naphthylmethyldiisobutylthiourea, $C_6H_5(C_{10}H_7)CHNHCSN(C_4H_9)_2$, formed clusters of slender radiating crystals from alcohol melting at 142°-143°. A nitrogen determination gave:

	Calculated for $C_{25}H_{32}N_2S$.	Found.
Nitrogen	6.93	7.22

Phenyl-α-naphthylmethylphenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHC_6H_5$, formed a difficultly soluble precipitate when the constituents were mixed in benzene. It was crystallized from a mixture of toluene and ethyl benzoate, whereupon colorless prisms melting at 185° were obtained. A nitrogen determination gave:

	Calculated for $C_{24}H_{20}N_2S$.	Found.
Nitrogen	7.60	7.64

Phenyl-α-naphthylmethylmethylphenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSN(CH_3)C_6H_5$, formed a fine, white crystalline powder which, on crystallizing from toluene, melted at 182°-183°. A nitrogen determination gave:

	Calculated for $C_{25}H_{22}N_2S$.	Found.
Nitrogen	7.32	7.35

Phenyl-α-naphthylmethylmetachlorphenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHC_6H_4Cl$, formed colorless, needle-like prisms from alcohol, melting at 172°-173°. A nitrogen determination gave:

	Calculated for $C_{24}H_{19}N_2ClS$.	Found.
Nitrogen	6.95	6.93

Phenyl-α-naphthylmethylmetanitrophenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHC_6H_4NO_2$, was difficultly soluble in alcohol from which it crystallized in the form of light yellow prisms. It melted at 191°, and a nitrogen determination gave:

	Calculated for $C_{24}H_{19}O_2N_3S$.	Found.
Nitrogen	10.17	10.10

Phenyl-α-naphthylmethyl-β-naphthylthiourea, $C_6H_5(C_{10}H_7)CH—NHCSNHC_{10}H_7$, gave colorless needles from toluene melting at 195°. A nitrogen determination gave:

	Calculated for $C_{28}H_{22}N_2S$.	Found.
Nitrogen	6.69	6.52

Phenyl-α-naphthylmethylphenylthiosemicarbazide was obtained from the isothiocyanate and phenylhydrazine in an alcoholic solution. Thus obtained, it melted at about 154°, solidified, and melted then at 174°-175°, with decomposition and effervescence. A recrystallization from alcohol gave needles which melted at 178°-179°. Evidently we have to deal here with a molecular rearrangement similar to that observed by Busch and Holzmann:[1]

$$C_6H_5(C_{10}H_7)CHNHCS(C_6H_5)N—NH_2 \rightarrow C_6H_5(C_{10}H_7)CHNHCSNH—NHC_6H_5.$$

Melting-point 154°. Melting-point 178°-179°.

An analysis of the material crystallized from alcohol gave:

	Calculated for $C_{24}H_{21}N_3S$.	Found.
Nitrogen	11.32	11.30

[1] *Ber. d. chem. Ges.*, 34, 320 (1901).

Di-α-naphthylmethane, $(C_{10}H_7)_2CH_2$.—The onlymethod given in Beilstein's "Handbuch" for the preparation of this hydrocarbon is that of Grabowski.[1] This method, according to our experience, gives a very poor yield (4 to 6 per cent.). By far the largest portion of the naphthalene in this process is converted into a difficultly soluble substance, the nature of which we did not stop to determine.

By means of the following method we have obtained yields over twice as great as by the above and with much less trouble.

Twenty-three grams of chlormethylacetate, CH_2COOCH_2Cl, 60 grams of naphthalene and 15 grams of fused zinc chloride (powdered) were mixed and heated on the steam-bath until the evolution of hydrogen chloride practically ceased. This required about three hours. The product was then washed with water, taken up with ether, and dried over calcium chloride. The ether was removed and all that came over below 300° was discarded. From this point the distillation was carried on as long as possible. The product above 300° was then distilled at 14 mm. pressure, whereupon most of the material boiled at 270°-272°. It had a strong blue fluorescence by reflected light and on standing a few hours it solidified. On crystallizing from alcohol 7 grams of the hydrocarbon were obtained melting at 99°-100°.

Di-α-naphthylmethylbromide, $(C_{10}H_7)_2CHBr$, was prepared from the hydrocarbon, obtained by both of the above methods, by brominating at 135°-145°. The bromide crystallized from benzene in needle-like prisms which melted at 181°-182°. It was very soluble in chloroform and sparingly soluble in ligroïn. A bromine determination gave:

	Calculated for $C_{21}H_{15}Br$.	Found.
Bromine	23.0	22.9

Di-α-naphthylmethylisothiocyanate, $(C_{10}H_7)_2CHNCS$. — The bromide was boiled in benzene with potassium thiocyanate for three days. The product, an oil, solidified on standing. It was then crystallized from alcohol and obtained in the form of colorless rectangular prisms, which melted at 124°-125°. A nitrogen determination gave:

	Calculated for $C_{22}H_{15}NS$.	Found.
Nitrogen	4.30	4.30

[1] *Ber. d. chem. Ges.*, 7, 1605.

Di-α-naphthylmethylphenylthiourea,
$(C_{10}H_7)_2CH—NHCSNHC_6H_5$, from the above rhodanide and aniline, when crystallized from ethyl benzoate, gave colorless needles melting at 225°-226°. It was only sparingly soluble in toluene and amyl acetate. A nitrogen determination gave:

	Calculated for $C_{28}H_{22}N_2S$.	Found.
Nitrogen	6.69	6.53

Di-α-naphthylmethylmethylphenylthiourea,
$(C_{10}H_7)_2CH—NHCSN(CH_3)C_6H_5$, from the isothiocyanate and methyl aniline, crystallized from toluene in fine colorless needles melting at 210°-211°. A nitrogen determination gave:

	Calculated for $C_{29}H_{24}N_2S$.	Found.
Nitrogen	6.48	6.59

Di-α-naphthylmethyl-β-naphthylthiourea,
$(C_{10}H_7)_2CH—NHCSNHC_{10}H_7$, separated in balls of needles from the alcoholic solution of its constituents. It crystallized from amyl acetate and melted at 218°-219°. A nitrogen determination gave:

	Calculated for $C_{32}H_{24}N_2S$.	Found.
Nitrogen	5.98	6.11

The following rhodanides were examined in order to complete the list of twenty compounds mentioned in the introduction.

1'-Thiocyanethylbenzene and Thioacetic Acid.—This thiocyanate, which may be viewed as methylphenylmethyl rhodanide, $CH_3(C_6H_5)CHSCN$, reacted smoothly with thioacetic acid and the product crystallized from alcohol, in which it was very soluble, in slender yellow prisms. It melted at 99°-100° and was soluble in alkali from which solutions acids precipitated the material unaltered. These properties and the following nitrogen determination show that this substance is an acetyldithiourethane, namely, $CH_3CONHCS.SCH(CH_3)C_6H_5$.

	Calculated for $C_{11}H_{13}ONS_2$.	Found.
Nitrogen	5.85	6.16

Isopropyl Thiocyanate and Thiobenzoic Acid.—Four grams of isopropyl thiocyanate and 5.4 grams of the acid were dissolved in 2 volumes of benzene and heated several hours on the steam-bath. On cooling, brilliant yellow plates separated. They were recrystallized from alcohol and melted at 74°-75°. The material was

soluble in alkali and was reprecipitated unaltered by acids. A nitrogen determination agreed with the calculated for *benzoyldithioisopropyl carbamate,* $C_6H_5CONHCS.SC_3H_7$.

	Calculated for $C_{11}H_{13}ONS_2$.	Found.
Nitrogen	6.11	6.08

These latter rhodanides are therefore both normal thiocyanates.

NEW HAVEN, CONN.,
April 12, 1902

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REFRACTIVE INDICES OF SALAD OILS—CORRECTION FOR TEMPERATURE.

BY L. M. TOLMAN AND L. S. MUNSON.

Received April 28, 1902.

IT IS almost always difficult to obtain exactly a definite temperature at which to make readings of refractive indices. A method and factor for making exact correction for this variation and also for making possible recalculations of determinations made at different temperatures is desirable.

Two factors are ordinarily used in this country to make this correction. One, 0.000176[1] for 1° C. for instruments reading index of refraction directly, and 0.55 scale division for 1° C. for the Zeiss butyrorefractometer, which has an empirical scale. As will be seen later, the former is considerably too small, and the latter was determined for butter-fat and is not correct for oils which have higher refractive indices.

As the butyrorefractometer is very largely used in this country, special attention should be called to a satisfactory method for correcting its readings for temperature. It must be remembered, however, that this discussion is limited to oils, and to the very limited number of oils given in Table III. Other substances and oils vary, and require different corrections for temperature. This instrument on account of its simplicity, ease of manipulation, and water jacket has acquired a very wide use but its empirical scale with division of varying value in refractive indices makes correction for temperature difficult and not exact unless, as is shown

[1] Wiley's "Principles and Practice of Agricultural Analysis," Vol. III, p. 334.

later, the scale readings are calculated to refractive indices and the correction factor applied to that, and then the corrected refractive index recalculated to scale division.

Table I[1] illustrates this variation of value of scale division in index of refraction.

TABLE I.

Scale division.	ND.	Difference.
0	1.4220	0.0080
10	1.4300	
40	1.4524	0.0069
50	1.4593	
90	1.4840	0.0055
100	1.4895	

Ten scale divisions from 0 to 10 equal 0.008 in index of refraction while from 90° to 100° they equal 0.0055. From this it is evident that if, as shown from Table III, the change in refractive index for 1° C. is practically a constant, then the change in scale division for 1° C. must be a variable.

Taking from Table III the average change in refractive index for 1° C. 0.000365, we find that it equals 0.46 of a scale division on reading from 0 to 10 on the scale and 0.66 of a scale division from 90° to 100° on the scale. Therefore on oils or fats, other things being equal, those that have a low reading will have a lower correction for temperature in scale divisions than those that have a high reading. This is illustrated in Table II, from readings made on a rape oil.

TABLE II.

Temp. °C.	Scale readings.	Change for 1° C. in scale divisions.	Change for 1° C. in refractive index.
2.8	82.0	0.60	0.000360
21.8	70.5		
21.8	70.5	0.57	0.000360
38.4	61.0		

The change in scale reading for 1° C. decreases as the temperature rises and the index of refraction falls, while the change in refractive index is constant.

This is also shown in columns 7 and 8 of Table III which give the change from the first reading to the second and from the second to the third. The higher the readings, the larger is the change in scale division for 1° C.

[1] Wiley's "Principles and Practice of Agricultural Analysis," Vol. III, p. 342.

TABLE III.

	Oils.	Temperature.	First reading.	Temperature.	Second reading.	Temperature.	Third reading.	Increase 1° C.	Increase for 1° C.	Change refractive index for 1° C.	Remarks.
		1	2	3	4	5	6	7	8	9	
23605	Olive	3.4°	76.5	22.0°	65.5	37 8°	56.5	0.59	0.57	0.000366	
506	Olive	3.2°	76.0	22.2°	64.8	36.8°	56.5	0 59	0.57	0.000366	
23460	Olive	3.2°	76.0	22.2°	65.0	43.3°	53.0	0.58	0.56	0.000360	
493	Poppyseed	9.0°	82.5	19.9°	75.6	41.0°	63.2	0.63	0.59	0.000369	Gave wide blue band, making it hard to read.
491	Corn	2.8°	84.5	21.8°	73.0	39.6°	62.5	0.60	0.59	0.000366	
498	Sunflower	3.0°	81.0	21.8°	69.5	39.0°	59.5	0.61	0.58	0.000369	
23624	Sunflower	3.0°	81.2	22.0°	70.0	39.0°	60.0	0.59	0.58	0.000364	
496	Rape	2.8°	82.0	21.8°	70.5	38.4°	61.0	0.60	0.57	0.000363	
490	Rape	3.4°	82.2	22.0°	71.0	38.8°	61.4	0.60	0.57	0.000364	
486	Mustard	2.8°	84.5	22.0°	72.5	38.0°	63.2	0.62	0.58	0.000360	
495	Black mustard	3.2°	84.5	22.0°	73.0	39.4°	63.0	0.61	0.57	0.000361	
487	Lard	3.0°	74.5	22.0°	63.4	37.6°	54.6	0.58	0.56	0.000363	
22434	Lard	3.0°	75.2	22.0°	64.0	39.2°	54.0	0.59	0.57	0.000372	
499	Peanut	3.0°	78.5	22.0°	67.2	37.2°	58.5	0.59	0.57	0.000365	
23656	Peanut	3.3°	76.0	22.0°	64.5	44.2°	52.3	0.61	0.55	0.000366	
492	Peanut and cottonseed	3.4°	82.0	22.0°	70.5	42.4°	58.8	0.61	0.57	0.000369	
489	Sesame	3.4°	81.2	22.0°	70.0	38.2°	60.5	0.60	0.58	0.000370	
436	Cottonseed	3.4°	81.5	22.2°	70.0	37.6°	61.2	0.61	0.57	0.000368	
	Average									0.000365	

The oils used were partly of known purity and partly commercial oils which had been tested for adulterants. The temperatures were regulated by a current of water passing through the instrument. As there are no compensating prisms the dispersion of the oils could not be corrected and with some of the oils, especially poppy-seed which has a high dispersive power, considerable difficulty was encountered in making an accurate reading.

In fact with most of these oils there is more or less dispersion which makes an exact reading impossible, which may explain the slight differences in the change in refractive indices, rather than that there is any actual difference. As the change in refractive index for change of temperature is so much more constant than the change in scale division, it gives a much more accurate means of correcting the readings of the butyrorefractometer than can be had by use of any factor of the scale divisions.

The reading in scale division can be calculated into index of refraction, the proper correction for temperature made, and the index of refraction obtained recalculated into scale divisions. This can be readily done by means of a table prepared by Winton.[1]

For corrections for a few degrees one may use the formula

$R = R' - X(T - T')$.

R = reading corrected to T.

R' = reading at T'.

T = desired temperature.

T' = temperature at which reading was made.

X = change in scale division caused by a change of temperature of 1° C.

$X = 0.55$ for butters which read from 40° to 50° on the scale; for oils that read from 60° to 70° it equals 0.58; for oils that read from 70° to 80° it equals 0.62. Olds[2] gave the correction for temperature for olive oil and sweet almond oil, as 0.000364 for 1° C., which agrees very exactly with the results shown in Table III. Some work by J. H. Long[3] corroborates these results. He found that the correction was practically a constant for the oils he examined, but gave a little higher correction, 0.0004. H. R. Proctor,[4] in his work on the relation between the specific gravity and refrac-

[1] *Conn. Expt. Station Report* (1900), Pt. 2, p. 143.

[2] *Wied. Ann.*, 10, 542 (1880); Landolt and Börnstein's Tables, p. 207.

[3] *Am. Chem. J.*, 10, 392 (1889).

[4] *J. Soc. Chem. Ind.*, 17, 1023 (1898).

tive index at different temperatures, has a large number of determinations of index of refraction at 15° C. and 60° C.

The following table of temperature corrections has been calculated by the writers from these results. Table IV shows remarkable agreement with Table III.

Oil.	Correction for 1° C. in refractive index.
Linseed	0.00037
Cotton	0.00037
Peanut	0.00037
Corn	0.00036
Sesame	0.00037
Olive	0.00037
Rape	0.00036

From these results it would seem that the correction for change in refractive index for the ordinary fats and oils is very uniform, about 0.000365 for 1° C.

THE PRODUCTION OF ACYLAMINES BY THE INTERACTION OF SODIUM SALTS OF MONOBASIC ACIDS AND AMINE HYDROCHLORIDES.

By Frederick L. Dunlap.

Received May 13, 1902.

During the course of some experimental work, I had occasion to try the action of sodium acetate on aniline hydrochloride. These two compounds reacted quite readily with the production of acetanilide. A brief study of this type of reaction was extended to analogously constituted bodies, the results of which experiments are given in this paper. This reaction was made use of with the sodium salts of acids containing both open and closed chains, and with alphyl- as well as with arylamines.

When the sodium salt of the monobasic aliphatic or aromatic acid is caused to react, under the influence of heat, the reaction proceeds as follows, R and R' being either an alphyl or aryl residue:

$$RCOONa + R'NH_2HCl = R'NHCOR + NaCl + H_2O.$$

In two of the experiments, conditions were varied to see the effect of temperature and mass on the yield of the resulting product, namely, in the cases where calcium and sodium acetates reacted with aniline hydrochloride. In all other cases, reaction

was brought about between molecular quantities. The calcium acetate mentioned above was the only salt other than a sodium salt made use of in this work.

No mention of such a reaction as has been outlined could be found in the literature; but after the experiments had been carried on for some time, it was found that this method had been the subject of the United States patent[1] for the manufacture of acetanilide from aniline hydrochloride and calcium or sodium acetate.

Inasmuch as this reaction took place so readily with the hydrochloride of the primary alkylamines, which we look upon as salts of substituted ammonia, there was every reason to expect that the reaction would also take place easily with ammonium chloride; and such was found to be the case, ammonium chloride reacting quite as readily as the alkylamine salts.

The reaction between the hydrochlorides of these primary alkylamines and the sodium salts of monobasic acids proceeds as follows: First, the splitting off of sodium chloride with the formation of free acid and free amine; second, the union of the amine and the acid; third, the breaking-down of the salt formed from the amine and the acid, under the influence of heat, to form the acylamine and water.

I. $RCOONa + R'NH_2HCl = NaCl + RCOOH + R'NH_2$.
II. $RCOOH + R'NH_2 = RCOONH_3R'$.
III. $RCOONH_3R' = RCONHR' + H_2O$.

In the cases where ammonium chloride was used, $R' = H$.

These stages are made sufficiently clear from the following facts: First, the formation of free acid is evidenced by the reaction resulting between sodium acetate and aniline hydrochloride, when these substances are ground together in a mortar, for a strong odor of acetic acid is developed. Then Lorin[2] has shown that when concentrated formic acid is heated in the presence of anhydrous sodium or potassium formate at 150°-155°, the formic acid decomposes into water and carbon monoxide. Formic acid alone decomposes at 160°, with the formation of hydrogen and carbon dioxide. When sodium formate and aniline hydrochloride were heated together in a sealed tube at 185°, no formamide was produced, but there was considerable gas pressure in the tube on

[1] U. S. Patents 574,395 and 574,396.
[2] *Jahresbericht*, (1876), p. 515.

opening it, due to the formic acid produced by the reaction undergoing decomposition in one, or perhaps both, of the ways indicated.

Sodium formate itself does not undergo decomposition until it reaches a much higher temperature[1]. Second, if free acid is produced by such reactions, free amine must also be produced. The production of the latter was easily distinguished in some of the experiments. The production of a free acid, say acetic, and of a free amine, for example aniline, must result in the formation of a salt—in this case aniline acetate. Third, the production of acetanilide from aniline acetate by means of heat, is a well known reaction.

As has already been stated, but two series of experiments were conducted to see the effect of temperature and mass on the yield of the resulting product. In some of the results obtained, the yield must have been very largely influenced by the fact that the mixtures were charged into the sealing tubes in a perfectly dry condition, thus precluding any very intimate contact of reacting masses. The following list shows the mixtures that were used, and the resulting products:

	Product.
Sodium acetate and aniline hydrochloride.....	Acetanilide
Calcium acetate and aniline hydrochloride.....	Acetanilide
Sodium acetate and *o*-toluidine hydrochloride...	*o*-Acettoluide.
Sodium acetate and ammonium chloride.....	Acetamide.
Sodium benzoate and aniline hydrochloride.....	Benzanilide.
Sodium benzoate and ammonium chloride.....	Benzamide.
Sodium benzoate and methylamine hydrochloride.	Methylbenzamide.
Sodium formate and aniline hydrochloride.....	

EXPERIMENTAL PART.

Sodium Acetate and Aniline Hydrochloride.—I. Molecular quantities of freshly fused sodium acetate and thoroughly dried aniline hydrochloride were heated, by means of an oil-bath, in a flask having a return condenser. The dry products were not intimately mixed before being introduced into the flask. Upon heating, the contents of the flask began to liquefy and turn dark. This mixture was heated for nearly three hours at 140°, and the acetanilide obtained amounted to 38 per cent. of the theoretical yield.

[1] *Ber. d. chem. Ges.*, 15, 1507 (1882).

II. This experiment was the same as the preceding one, except that the mixture was heated for seven and a half hours on a steam-bath. Yield of acetanilide, 23 per cent. of the theory.

III. Molecular quantities of sodium acetate and aniline hydrochloride were ground together in a mortar, in order to give an intimate mixture. In a few moments after the dry salts began to be triturated, the resulting product became pasty, and finally semi-fluid. This semi-fluid mass, which smelled strongly of acetic acid, was introduced into a sealing tube, and then heated for seven hours at 120°. After this treatment, the contents of the tube were purple in color, and there was no pressure on opening the tube. Yield, 54 per cent.

IV. This experiment was carried out similarly to the preceding one, except that twice the amount of sodium acetate was employed. This mixture was heated for three hours at 165°, and a yield of 71-72 per cent. was obtained.

V. Same as No. IV, except that the temperature was held at 120° for six hours. Yield, 65 per cent.

Calcium Acetate and Aniline Hydrochloride.—I. Molecular quantities, intimately mixed in a mortar, were heated in a sealed tube for five hours at 197°. Yield of acetanilide, 58 per cent.

II. Same as preceding experiment, except that the temperature of heating was 160°, while the duration of heating was but four hours. Yield, same as in No. I.

III. Where twice the amount of aniline hydrochloride was used, *i. e.*, theoretically enough of the hydrochloride to decompose the calcium acetate, and the mixture heated in a sealed tube for seven hours at 150°, the yield of acetanilide was nearly 50 per cent.

Sodium Acetate and o-Toluidine Hydrochloride.—Molecular quantities of these compounds were ground together in a mortar to mix them intimately. On grinding, this mass acted similarly to the sodium acetate and aniline hydrochloride mixture, *i. e.*, became at first moist and pasty, and finally semi-fluid. This mass was then charged into a sealing tube and heated for eight hours at 320°. There was no pressure on opening the tube. The tube was filled with a crystalline product which was purified by crystallization from benzene. The pure product melted at 109°. Alt[1] gives the melting-point of *o*-acettoluide as 110°, and

[1] *Ann. Chem.* (Liebig), 292, 319 (1889).

Wroblewsky[1] as 107°. From its physical and chemical properties, this body was easily recognized as *o*-acettoluide. Due to loss of mother-liquors, no yield was calculated.

Sodium Acetate and Ammonium Chloride.—Molecular quantities of these compounds were ground together as in the previous cases mentioned. During this process of grinding, the production of free ammonia was readily detected by its odor. This mixture was heated in a sealed tube for five hours at 240°. There was no pressure on opening the tube. The contents of the tube were partly liquid and partly solid; it was washed out with alcohol, the insoluble portion filtered off, and the alcoholic solution fractioned. A yield of about 40 per cent. of acetamide was obtained.

Sodium Benzoate and Aniline Hydrochloride.—Molecular quantities of these substances were intimately mixed in the usual manner. During the mixing the mass became damp, and the odor of free aniline was strongly developed. After heating in a sealed tube for four hours at 245°, the product was dark-colored, and the tube contained a crystalline product. After washing out the contents of the tube with cold water, then treating with dilute hydrochloric acid, the residue was treated with bone-black in an alcoholic solution and allowed to crystallize. When pure, the product melted at 160°; it was easily identified as benzanilide. Yield, 30 per cent.

Sodium Benzoate and Ammonium Chloride.—Molecular quantities, after mixing, were heated for eight hours at 260°. The contents of the tube were washed thoroughly with small quantities of cold water, then recrystallized from boiling water. This product by repeated crystallization could not have its melting-point raised beyond 125°. The melting-point of benzamide is usually given as 128°; for example, it is so given in Gattermann's "Praxis des organischen Chemikers". A sample of Kahlbaum's benzamide melted at 125°, and repeated crystallization would not raise it higher.

Apropos of the question of the discrepancy in the melting-point of benzamide, it is of interest to note the effect on the melting-point by the use of the two types of melting-point apparatus usually employed in these determinations. These two types, which are fully described in Gattermann's "Praxis des organischen Chemikers," differ essentially in the fact that the first has a greater

[1] *Ann Chem.* (Liebig), **168**, 162 (1873).

or less portion of the thermometer enclosed by a glass tube, the liquid in which the thermometer bulb is placed being heated with a free flame. In the second type, moreover, the thermometer stem is exposed directly to the air, the small beaker in which the bulb is placed being separated from the flame by wire gauze. In the first type heat is conveyed through the liquid by the convection currents; in the second, convection currents are done away with, as far as possible, by constant agitation with a hand stirrer.

In the first type mentioned (a 250° milk glass thermometer being used) benzamide melts from three-quarters to one degree higher than when the determination is made with the second type. The higher the melting-point, the greater will be the discrepancy in the readings between these two types. The higher reading in the first method is easily accounted for by the fact that the temperature of the air between the glass envelope and the thermometer is at a higher temperature than the air surrounding the thermometer stem in the second type. This must result in a higher reading, and one that is therefore nearer to the corrected melting-point. The melting-points given in this paper were made according to the second method.

Sodium Benzoate and Methylamine Hydrochloride.—When molecular quantities of these substances were ground together, the odor of methylamine was developed. The mixture was heated in a sealed tube for twelve hours at 280°, and on opening the tube, while there was no pressure, there was a slight odor of methylamine. The tube was filled with a pale yellow viscous liquid and some crystals. On shaking up the contents of the tube with cold water, this yellow liquid solidified. It was filtered, dried, dissolved in ether, and precipitated out with low boiling ligroïn. This method of purification is much preferable to the one given by van Romburgh,[1] who purified methylbenzamide by crystallizing from hot water. The yield of methylbenzamide obtained was 32 per cent. of the theory and it had a melting-point of 78°.

Sodium Formate and Aniline Hydrochloride.—When these compounds, intimately mixed, were heated in a sealed tube to 185° for seven hours and then cooled, the tube, on opening, exhibited considerable gas pressure and was filled with a dark liquid (aniline). From the contents of the tube no formamide was obtained.

CHEMICAL LABORATORY,
UNIVERSITY OF MICHIGAN.

[1] *Rec. trav. chim. Pays-Bas*, 4, 388 (1885).

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

AN INVESTIGATION OF WOOD TAR FROM THE DOUGLAS FIR, "PSEUDOTSUGA TAXIFOLIA."[1]

BY H. G. BYERS AND PAUL HOPKINS.

Received May 17, 1902.

THE Douglas fir, better known as Oregon Pine, grows only upon the humid western slopes of the Cascade range. Its great size and its value as a source of timber makes it an important part of the natural wealth of the northwest. A number of attempts have been made to make use of the waste products in the mills of this state but without very marked success. The quantity of material destroyed by our mills is enormous. There are mills on Puget Sound which have been burning their waste for thirty years and during all that time the fires have not been out.

In view of these facts and because of almost numberless requests for information concerning the products of distillation of fir wood we decided to make some little investigation upon that subject in order to get data that would afford a comparison between our wood and that used in distillation processes in other places.

The Rainier Tar Company, of Seattle, kindly placed at our disposal a large steel retort capable of holding about three-fifths of a cord of wood. In this retort two carefully regulated runs were made. The products of the distillation were condensed in a 4-inch copper worm 125 feet in length, surrounded by cold water. All the products were carefully measured except the gas, which was estimated by difference.

The material used in the distillation was partially seasoned fir wood taken from the "butt cuts" of trees. It was cut into 2-foot lengths, weighed, and placed in the retort, which was held at as constant a temperature as possible. Not having a pyrometer at our disposal we arrived at an approximation of the temperature by means of small bars of metals placed within the retort so that the maximum temperature could be determined. In the case denominated "low run" in the following discussion at no time did the temperature rise above 420° C., the melting-point of zinc, while in

[1] *Pseudotsuga mucronata* (Sargent's *silva*).

the "high run" the temperature never exceeded 700°, the melting-point of aluminum.

The time required to complete the distillation of a charge was about twelve hours, and the quantity used was about half a cord and weighed 2,500 pounds.

The results of these distillations are as follows:

	High run.	Low run.
Pyroligneous acid	34.0	47.5
Tar	17.7	7.5
Charcoal	29.0	30.0
Gas	19.3	15.0
Total	100.0	100.0

The high percentage of tar in the high run was due to the fact that it contained an abnormal quantity of water which in the course of several weeks settled out gradually. Referring the weight of water-free tar to the wood we have 6.37 per cent. for the high run and 6.00 for the low run.

PYROLIGNEOUS ACID.

The pyroligneous acid produced in the distillation was of a rich red color, that from the low run being slightly the darker. The specific gravity of the low run was 1.025; that of the high run was 1.020. The methyl alcohol was determined by conversion into methyl iodide by means of phosphorus tri-iodide. The percentages were: for the high run 2.95; for the low run 4.16 per cent. (volume). The percentage of acetic acid was determined by direct titration and found to be 2.90 per cent. for the high run and 3.47 for the low run.

TAR.

The tar was fractionated and the oil which distilled below 150°, the light oil, was investigated a little more fully than the other portions. A discussion of its constituents will be found at the close of this article. The creosote oil boiling between 150° and 250° was separated and the residue weighed as pitch.

The results of this separation are as follows:

	High run.	Low run.
Specific gravity	1.060	1.075
Watery distillate (pyroligneous acid)	64.0	20.0
Light oil	8.0	18.0
Creosote oil	10.0	23.0
Pitch	18.0	39.0

Because of the great amount of water in the one sample a more accurate comparison of the composition may be gained by referring these values to water-free tar as:

	High run.	Low run.
Light oil	22.2	22.5
Creosote oil	27.8	28.7
Pitch	50.0	48.8

The creosote in the creosote oil was separated in the usual way and found to be 17 per cent. of the oil or 5 per cent. of the tar. The percentage of guaiacol in the creosote was also determined and found to be about 9.5 per cent.; the method used was that given in Allen's "Commercial Organic Analysis," Vol. II, Part II, p. 284. The creosote is almost colorless, has a smoky aromatic odor and a specific gravity of 1.065. It seems almost identical with the product of beech-wood tar. The pitch from the tar is black or very dark brown and resembles closely in appearance coal-tar pitch but has not the same odor or taste.

Since great quantities of Stockholm tar are imported for the local market and it commands a high price, it seemed worth while to compare our product with that and also with pine tar. We found that by removing the water and a certain amount of the light oil, a tar could be obtained which resembles Stockholm tar very closely. The color suffers somewhat in the redistillation yet the tar as obtained can not be otherwise distinguished from Stockholm tar, even by the tests usually given for identification of the latter.[1] A fair idea of the variations may be gained from the following table:

	Fir tar.	Stockholm tar.	Pine tar.
Color	Black (almost).	Brownish black.	Brown.
Odor	Smoky but characteristic.	Smoky.	Resinous.
Consistency	Sirupy.	Sirupy.	Viscid.
Specific gravity	1.100	1.090	1.110
	Per cent.	Per cent.	Per cent.
Light oil	3	3	5
Creosote oil	34	30	40
Pyroligneous acid	4	5	2
Pitch	59	62	53
Hardness of pitch	Brittle.	Less brittle.	Soft.
Color of pitch	Black.	Black.	Brown.

[1] Allen's "Commercial Organic Analysis."

The light oil which is separated from the tar by this redistillation has a specific gravity of 0.945 and when freshly distilled is of a clear amber color but darkens markedly on standing.

THE CHARCOAL.

There was no attempt made to distinguish between the samples of charcoal made at the different temperatures. The quantities were nearly the same and they were similar in appearance. The coal is soft and retains the porous structure of the wood. It is, however, remarkably free from ash.

THE GAS.

No attempt was made to analyze the gas given off in this distillation and its amount was determined by difference. This gas is, however, utilized in the processes of the refining of the wood products. It is non-illuminating and hence cannot be used directly as an illuminant, except in Welsbach burners, in which it gives an excellent light. A series of tests was made on this subject in the city of Tacoma and a sample of the gas was sent us for analysis. The temperature at which it was produced was much higher than those of our experiments and the retort was arranged to decompose almost totally all the tar produced. The results are as follows:

	Per cent.
Light hydrocarbons	6.3
Heavy hydrocarbons	0.0
Methane	7.3
Carbon monoxide	28.8
Hydrogen	30.6
Carbon dioxide	12.3
Nitrogen	14.7

THE LIGHT OIL.

In addition to the foregoing experiments we decided to compare our light oil with that obtained from hard woods as given in an investigation by G. S. Fraps.[1]

This was not fully carried out by reason of lack of time but a few points of interest were developed. Only that portion of the oil boiling below 140° was used. Fifteen liters of the light oil were first fractioned into six fractions—below 75°; 75°-90°; 90°-105°; 105°-120°; 120°-135°; 135°-150°. These portions were then

[1] *Am. Chem. J.*, 25, 26.

fractioned, through a Hempel tube, five times and the fractions collected for every five degrees.

It was found that a small portion passed over before 50° was reached and indeed a little before 40° but this is included in the portion 40°-50°. The following table shows the result of this fractionation in percentage of total oil:

Fraction.	Per cent.	Fraction.	Per cent.
40°- 50°	0.37	105°-110°	0.87
50°- 55°	0.47	110°-115°	0.43
55°- 60°	0.77	115°-120°	0.53
60°- 65°	0.55	120°-125°	0.40
65°- 70°	0.62	125°-130°	0.37
70°- 75°	0.70	130°-135°	0.002
75°- 80°	0.57	135°-140°	0.73
80°- 85°	0.93	40°-140°	13.68
85°- 90°	0.94		
90°- 95°	1.40		
95°-100°	1.37		
100°-105°	0.97		

The table shows five points of accumulations of distillate but they are not so marked nor is the percentage of oil coming over below 140° nearly so great as in the oil investigated by Mr. Fraps. The color of the oily distillates varied from colorless to almost black and always darkened upon standing, but the change was not regular.

SOLUBILITY.

The solubility of the fractions was determined by shaking 2 cc. of the oil in a graduated pipette with 10 cc. of water, and determining the loss of volume. The results follow:

Fraction.	Solubility. Per cent.	Fraction.	Solubility. Per cent.
40°-50°	55	85°-90°	30
50°-55°	52	90°-95°	27
55°-60°	50	100°-105°	20
60°-65°	44	105°-110°	16
65°-70°	40	110°-115°	12
70°-75°	35	115°-120°	12
75°-80°	34	120°-125°	10
80°-85°	32	125°-130°	10
		130°-135°	9
		135°-140°	9

It will be noticed that the solubility of this oil is greater for corresponding fractions than in the hard wood oil.

KETONES AND ALDEHYDES.

The ketones and aldehydes were removed from each fraction by shaking with a concentrated solution of acid sodium sulphite, keeping the mixture cool during the reaction. The crystalline precipitates were filtered by suction through muslin, and dried. A second precipitation with sulphite was always attempted. As in the hard oil, the precipitates from the lower fractions were distinctly crystalline and became more gelatinous with the higher fractions, but, curiously, when the higher fractions were reached, *viz.*, from 100° upward, the precipitates became crystalline again. In filtering the lower fractions a strong odor as of acrolein was developed.

The precipitates contained very small quantities of aldehydes. Assuming that half the weight of the dried precipitate is the volume of the ketone the following approximation is reached.

Fraction.	Ketones. Per cent.	Fraction.	Ketones. Per cent.
40°–50°	2.2	95°–100°	1.1
50°–55°	5.7	100°–105°	1.1
55°–60°	9.7	105°–110°	1.0
60°–65°	6.3	110°–115°	2.5
65°–70°	2.2	115°–120°	2.2
70°–75°	3.9	120°–125°	1.7
75°–80°	2.2	125°–130°	1.4
80°–85°	2.1	130°–135°	1.0
85°–90°	4.3	135°–140°	4.4
90°–95°	1.6		

It will be seen that while there is not nearly so large a percentage of ketones in the fir as in the hard oil yet there are marked accumulations at 55°-60° (this is probably acetone), at 70°-75°, at 85°-90°, and at 135°-140°. We attempted to separate the ketones from the sulphite fractions, but the quantities were too small to be of use in further investigation. However, in the fraction 125°-130° a test was made for mesityl oxide which was not found by Mr. Fraps in the hard oil. The solution was distilled with strong caustic soda and a strong odor of peppermint was developed, showing the possible presence of mesityl oxide.

ETHEREAL SALTS.

The residual oil after removal of the ketones was dried and fractionated. The fractions were shaken with a caustic soda solution (1:4) for fifteen to twenty hours. To accomplish this the

glass-stoppered bottles were fastened to the face of a wooden pulley about 8 inches in diameter which made nine revolutions per minute. The oils were measured before and after saponification and the loss in volume was considered to be due to the saponification of ethereal salts. This loss was for each fraction as follows:

Fraction.	Per cent.	Fraction.	Per cent.
40°–50°	20	90°–95°	18
50°–55°	23.5	95°–100°	20
55°–60°	27	100°–105°	19
60°–65°	24	105°–110°	13.9
65°–70°	25	110°–115°	17.6
70°–75°	25	115°–120°	15.6
75°–80°	18.5	120°–125°	20.7
80°–85°	31	125°–130°	38.5
85°–90°	15.5	130°–135°	25.4
		135°–140°	27.1

It will be observed that there are marked accumulations at certain temperatures and also that there is no marked decrease in the amount of oil saponified as the boiling-point of the fraction rises. In the higher boiling fractions a gummy solid of a yellow color was formed, which while insoluble in water dissolved easily to a purple solution in nitric, hydrochloric, or sulphuric acids. This color was not destroyed by boiling but disappeared on standing and on addition of water. No attempt to discover its nature was made.

The caustic soda solutions of the ethereal salts were distilled to remove alcohols. No odor of ammonia was developed.

The alcoholic distillates were all found to contain methyl alcohol by the test of Mulliken and Scudder.[1] The alcoholic distillates were also treated with iodine and caustic potash and always gave a decided test for ethyl alcohol.

The acids were now freed by addition of sulphuric acid and distilled.

The silver salts precipitated from the fraction boiling at 40°-50° gave 68.74 per cent. silver. Calculated percentage of silver in silver formate is 70.59; in silver acetate 64.66. The acid was therefore probably a mixture of the two, since methyl formate boils at 30.4° and some of the oil passed over before that temperature was reached. The silver salt of the 50°-55° fraction gave:

[1] *Am. Chem. J.*, 24, 444.

	Found.	Formic acid.	Acetic acid.
Percentage of silver	65.44	70.59	64.66

This result we take to indicate the presence of ethyl formate (54.9°) and methyl acetate (57.3°).

The silver salt from fraction 55°-60° gave 64.99 per cent. of silver (calculated for acetic acid, 64.66). It hence consisted almost entirely of methyl acetate (57.3°).

The presence of acetic acid was also indicated by qualitative tests in fraction 70°-75°. Satisfactory results from the silver salt were not obtained because of the small quantity at our disposal.

The same statements apply to fractions 75°-80° in which the boiling-point and odor indicate the presence of methyl propionate (79.5°).

From the fraction 102°-105°, by acidifying with sulphuric acid, an oil separated which was by odor butyric acid and indicates the presence of methyl butyrate (102.3°).

The investigation was necessarily interrupted at this point but will probably be taken up at some future date.

There seems to be enough of interest in the wide difference between this oil and that from other varieties of wood to warrant further investigation.

SEATTLE, WASH.,
March 3, 1902.

INVESTIGATION OF THE OIL OF THE RED ELDERBERRY, "SAMBUCUS RACEMOSA ARBORESCENS."

BY H. G. BYERS AND PAUL HOPKINS.

Received May 17, 1902.

ON the western slopes of the Cascade Mountains and on the lowlands about Puget Sound grow great quantities of a red elderberry which, by reason of its large size, is denominated a variety of the species *racemosa*. The berries are a bright crimson and serve as food for birds but because of an unpleasant odor and the presence in them of a considerable quantity of a yellow oil are not used by the people as food nor are they converted into wine.

An investigation of this oil was made with the following results. From about 10 gallons of the berries it was possible to get about 500 cc. of the oil by pressing the juice from berries and ex-

tracting with ether the layer of crude oil which rose to the surface of the liquid. The oil as obtained from the ether solution by spontaneous evaporation is of a light yellow color but darkens markedly on standing or when the ether is evaporated by means of a water-bath.

The oil has a specific gravity of 0.9072 at a temperature of 15° C. It solidifies at —8° and melts at about 0°. It has no definite boiling-point but decomposes when distilled even at a pressure of 20 mm. It proved to be a mixture of the glycerides of the fatty acids and contains 6.65 per cent. free acid calculated as oleic acid. Because of a marked resemblance to olive oil a very careful determination of its constants and composition was made.

Unsaponifiable Matter.—The unsaponifiable matter of the oil, which contained the characteristic odor of the oil, formed 0.66 per cent. of the whole. It crystallizes in light yellow hexagonal plates.

Glycerol.—The fats were saponified and the glycerol determined, the amount being 11.4 per cent.

Fatty Acids.—The lead salts of the acids were made and thoroughly extracted with ether in a Soxhlet apparatus. The insoluble residue was converted into its barium salt and crystallized from alcohol in three fractions. These fractions gave the following results when their barium content was determined as barium sulphate.

	I.	II.	III.	Calculated for palmitic acid, $C_{16}H_{32}O_2$.
Percentage of barium	21.06	21.24	20.14	21.17
	21.11	21.21	20.13	

The crystals from the first two fractions were white plates. The third fraction was discolored by the impurities of the mother-liquor. The oil evidently contains no saturated fatty acid save palmitic acid.

The solution of the lead salts in ether was fractionally crystallized and converted into the barium salt. The barium salt was refractionated and the barium determined in the first fraction.

		Calculated for oleic acid, $C_{18}H_{34}O_2$.
Percentage of barium.....	19.46	19.59
	19.38	

The iodine absorption of the fatty acid from this fraction was also 90.6 and 89.5, the calculated value for oleic acid being 90.07.

A number of fractional precipitations of the potassium salt of the mixed acids were made from a weakly ammoniacal solution by means of barium chloride.

The iodine numbers of the free acids from these fractions were:

Fraction.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Iodine number.	21.0	36.2	88.2	89.3	87.3	90.6	111.3	120.6
Quantity of salt	2.0	1.2	1.5	1.0	1.0	0.8	0.5	2.0

The fatty acid from VII and VIII was highly colored and somewhat impure from oxidation, yet the results indicate the presence of an acid, probably linoleic, having an iodine absorption greater than that of oleic acid. If linoleic acid, it is present to an extent of not less than 7-8 per cent.

The presence of soluble acids was determined by the method of Muter.[1] The Reichert-Meissl number being but 1.54, thus showing the practical absence of butyric or other volatile acid, the results of the titrations were calculated to an acid having a molecular weight of 136, which is the mean of the molecular weights of capric, caprylic, and caproic acids. The results showed the presence of 2.95 per cent. of these acids.

The quantity of palmitic and oleic acids was determined by Lang's "Modification of Muter's Method".[2] The results show oleic acid and linoleic acid 72 per cent.; palmitic acid 21.66 per cent. The saponification equivalent was found to be 209.3.

The Hehner number is 91.75.

From the results indicated in the foregoing discussion the properties and composition of the oil are as given below. For convenience of comparison the corresponding values for olive oil are given in parallel.

	Elderberry oil. Per cent.	Olive oil. Per cent.
Palmitin	22.0	28.0
Olein and linolein	73.6 { 92.2 / 7.8 }	72.0 { 93 / 7 }
Caprin, caproin and caprylin	3.0	
Unsaponifiable matter	0.66	

[1] Allen's "Commercial Organic Analysis," Vol. II, Part I, p. 189.

[2] *Pharm. J.*, 59, 61.

	Elderberry oil.	Olive oil.
Specific gravity	0.907	0.914–0.917[1]
Solidifying point	—8°	2°
Melting-point of fatty acids	38°	26°
Saponification equivalent	209.3	191.7
Iodine number	81.44	80–82
Hehner number	91.75	94.03
Reichert-Meissl number	1.54	1.50
	Per cent.	Per cent.
Free acid	6.65	8.07

SEATTLE, March 14, 1902.

A VOLUMETRIC METHOD FOR THE ESTIMATION OF SULPHURIC ACID IN SOLUBLE SULPHATES.

BY YASUJURO NIKAIDO.

Received September 12, 1901.

THE method is based on the following reactions:

(1) $K_2SO_4 + Pb(NO_3)_2 = PbSO_4 + 2KNO_3$.

(2) $2KI + Pb(NO_3)_2 = PbI_2 + 2KNO_3$.

Under proper conditions it was found that lead salts will not react with iodides in the presence of sulphates until all the sulphuric acid has been precipitated by the lead, whereupon the yellow color of the lead iodide becomes visible. It is, therefore, possible to use potassium iodide as an indicator for the end reaction between lead and sulphuric acid.

To test the accuracy of the method, N/10 solutions of lead nitrate and of potassium sulphate were used. Then 10 cc. of the potassium sulphate solution were taken, about 0.2 gram of potassium iodide added and the solution was titrated with a lead nitrate solution. It was found that on adding lead nitrate, lead iodide was first formed, imparting a yellow color to the solution. This color quickly disappears, owing to the formation of lead sulphate. As soon as all the sulphuric acid is precipitated the yellow color becomes permanent. In water solutions alone, however, the reaction is not complete, lead sulphate being somewhat soluble in water and the yellow color of the lead iodide showing slightly, even when an excess of potassium sulphate is present.

To avoid this, it was determined to try the reaction in an alco-

[1] Meyer and Jacobson: "Lehrbuch," Vol. I, p. 594.

holic solution, and for this purpose another 10 cc. of the potassium sulphate solution were taken together with about 0.2 gram of potassium iodide. Alcohol was then added until a slight precipitate of potassium sulphate was formed, and then the lead nitrate solution was carefully added. It was found that the color of lead iodide appeared just about when 10 cc. of lead nitrate solution had been added.

Experiments were made to find out in what strength of alcohol the reaction best takes place. Since in water alone it is impossible to obtain any satisfactory results, 25 per cent. alcohol was first used. With this, it was also impossible to obtain good results. Then a titration was made using 35 per cent. alcohol, but still the results were not satisfactory. In 40•per cent. alcohol the results were fair, but the reaction took place very slowly. In 50 per cent. alcohol, the results were fairly satisfactory, although the reaction was still slow. The results obtained from the titrations in 60 per cent. alcohol were satisfactory, and the reaction was moderately rapid. The titrations in 65 per cent. alcohol gave very satisfactory results, and the reaction went quite rapidly with the following results:

N/10 potassium sulphate solution. cc.	N/10 lead nitrate. solution. cc.
5.00	5.02
10.00	10.05
11.25	11.22
19.97	20.01
Average 1.00	1.0017

The results from the titrations in 70 per cent. alcohol were obtained in the same manner as in the 65 per cent. alcohol. It was found at this point, *viz.*, with 70 per cent. alcohol, or over, the reaction began to go more slowly and to become increasingly difficult to complete, owing to the insolubility of potassium sulphate in alcohol. The experiments show therefore that the reaction goes best in alcoholic solutions from 50 to 70 per cent.

Experiments were made to find out what effect various acids have upon the reaction. It was found that no satisfactory results could be obtained in the presence of free nitric acid, since it liberates iodine from potassium iodide and makes it difficult to see the color of the end reaction. In the presence of hydrochloric acid,

the reaction does not take place normally, because lead iodide is converted into a pale yellow compound (probably a double halogen salt of lead) which is not decomposed by neutral sulphates. The same compound is formed when a large quantity of chlorides is present. Small quantities of chlorides do not affect the titration. In the presence of free acetic acid the reaction takes place regularly and satisfactorily, but sodium acetate interferes with the titration, owing to the very considerable solubility of lead iodide in sodium acetate. The titrations were made also in the presence of free oxalic and tartaric acids. In the oxalic acid solution lead was precipitated, but not in the tartaric acid solution. In presence of potassium tartrate, lead was precipitated.

To determine the applicability of this method to stronger solutions of sulphates, a N/2 solution (43.47 grams per liter) of potassium sulphate was used. Portions of this solution were titrated with an N/2 solution (82.5425 grams per liter) of lead nitrate. It was found that in this case the titration was most satisfactory, using 50 per cent. to 60 per cent. alcohol.

The results were as follows:

N/2 potassium sulphate solution. cc.	N/2 lead nitrate solution. cc.
10.82	10.87
20.07	20.10
30.22	30.20
40.35	40.30
Average 1.00	1.00

Having in the manner indicated determined the accuracy of the method under the conditions mentioned, its applicability for the estimation of sulphuric acid in other sulphates was next tried. The substances used were magnesium sulphate, zinc sulphate, ferrous ammonium sulphate, copper sulphate, manganous sulphate, ferrous sulphate, and ferric ammonium sulphate.

In the titration with ferrous ammonium sulphate a few drops of acetic acid were added to prevent the formation of insoluble basic compounds. In the case of copper sulphate the copper was precipitated with zinc or aluminum and the titration carried out as usual after acidifying the solution with acetic acid in order to prevent the formation of precipitates of basic sulphates.

In the case of ferric ammonium sulphate, the iron was precipi-

tated with potassium hydroxide. The solution and precipitate were then transferred to a graduated flask and made up to a definite volume. The precipitate was allowed to settle and an aliquot part of the supernatant solution was taken and acidified with nitric acid, evaporated to dryness to expel free nitric acid, dissolved in water, alcohol added, and the solution titrated with lead nitrate. The error due to the volume of the ferric hydroxide is negligible in an N/10 solution in comparison with the errors of titration. In these determinations, pure substances which were obtained by recrystallization, and with each, semi-normal solutions were used. The results in all these titrations were fair and satisfactory.

The following precautions should be carefully observed. The titrations should never be made in warm solutions as lead iodide is soluble in hot water. The titrations should not be made in a large volume of solution as lead iodide is slightly soluble even in cold water.

It is probable that the method is applicable to all soluble sulphates, provided:

(1) That the operation is carried out in dilute alcohol, that is, 50-70 per cent. alcohol in case a tenth-normal solution of lead nitrate is used, and 50-60 per cent. alcohol in case a semi-normal solution of lead nitrate is used.

(2) That nitric acid, hydrochloric acid, sodium acetate and substances that will form insoluble compounds with lead are avoided.

(3) That in the case of colored sulphates, the base which gives color to the compound is removed by precipitation, *e. g.*, in the case of copper sulphate, the copper is precipitated, using zinc or aluminum; in the case of ferric ammonium sulphate, the iron is precipitated with potassium hydroxide.

(4) That in the case of the sulphates of the heavy metals, such as ferrous sulphate, ferrous ammonium sulphate, zinc sulphate, etc., a few drops of acetic acid are added to prevent the formation of basic sulphates.

(5) That the titrations are made in small volumes of cold solution, using about 0.2 gram of the potassium iodide to each 25 cc. of the solution.

Finally, it may be claimed for the method here proposed, that its

accuracy, rapidity, ease of manipulation and general applicability should render it more satisfactory than any of the previously known volumetric methods for the estimation of sulphuric acid.

The method may also be used for the estimation of lead in soluble compounds of lead by reversing the operation.

A PRELIMINARY NOTE ON THE OIL OF MILFOIL.

BY A. B. AUBERT.

Received April 30, 1900.

THE specimen examined was distilled by Metzner and Otto, of Leipzig. It is of a dark bluish green color and has a mild and pleasant odor. Specific gravity at 22° equals 0.9217. Refractive index, 1.506 at 20°. It is soluble in absolute alcohol, ether, xylene and chloroform; also in about 6.5 volumes of 95 per cent. alcohol with a slight residue of brownish colored oil.

It was distilled under reduced pressure with the following results:

One hundred volumes of the oil yielded:

7 parts by volume between 170°-190°.
17 parts by volume between 190°-210° (sp. gr. 0.900).
50 parts by volume between 210°-220° (sp. gr. 0.907).
9 parts by volume between 220°-235° (sp. gr. 0.936).
3 parts by volume above 235°.

The residue, constituting 14 parts, remaining in the flask was a semi-solid, dark olive-brown, waxy substance, hardly soluble in cold alcohol, partly soluble in boiling alcohol, yielding a dark yellow-brown solution. The insoluble residue was of a greenish brown color, somewhat resembling paraffin in consistency. By evaporation of the alcoholic solution a dark yellow-brown pitch was obtained.

The oil has a slightly acid reaction.

The products of distillation gave the following reactions:

170°-190°, slightly acid.
190°-210°, nearly neutral.
210°-220°, nearly neutral.
220°-235°, slightly acid.

(This distillate contained products of decomposition.)

That portion distilling between 170°-190° was tested for cineol,

with no very satisfactory results, the conclusion being that but a small amount of cineol is present.

The oil was examined for aldehydic constituents with sodium bisulphite. A slight precipitate formed which, upon decomposition with caustic potash, yielded traces of a substance having a faint odor somewhat similar to that of cedar wood.

A test was made for acids, but the quantity present was too small to give any definite results.

No sulphur compounds were detected. All the distillates exhibited traces of blue color. That portion distilling between 210° and 220° had a color very similar to that of a solution of copper sulphate, while that coming over at 220°-235° was much deeper in color but of a greenish blue shade.

The blue distillate (210°-220°) was redistilled, the greater part passing over at 214°. This was put away in a tightly corked bottle and after about a year and a half was examined. During that time its color had become quite light and changed to a yellowish green, though it had been carefully kept in darkness.

The ultimate analysis gave the following results:

	Oil. Gram.	C. Gram.	H. Gram.
No. I.....	0.3691	0.288	0.0400
No. II.....	0.3302	0.2886	0.0406

The molecular weight determination by the boiling-point method gave as results 164.5 and 165, which would correspond to the formula $C_{12}H_{20}$. The above determinations were performed by Mr. C. D. Holley, M.S., one of my former students.

The rotary power is —14.2° for 100 mm. tube. Refractive index, 1.492. It boils at about 254° (uncorr.) at 754.8 mm. pressure, undergoing slight decomposition. This substance exhibits most of the reaction of the terpenes.

A small quantity (5 cc.) was diluted with alcohol and ether (20 cc. each), kept cool, and bromine slowly added. The action was quite energetic, the light yellowish green solution soon changing to very dark green.

The alcohol and ether were driven off in a warm closet, leaving a greenish black pitchy residue which continued to emit hydrobromic acid for a long time. Ten cc. were diluted with 30 cc. of benzene, kept cool, and a steady current of dry hydrochloric acid gas passed through for an hour and a half. It was, at

first, quite rapidly absorbed, the liquid becoming red-purple and finally purplish brown. Upon evaporation of the benzene a dark brown, viscid liquid remained. A few drops were placed upon a watch-glass and several scales of iodine added For a moment no action was noticed. Very soon however a violent reaction set in, considerable of the iodine being vaporized thereby. The result of the reaction was a dark, sticky, resinous mass.

The remaining quantity of the distillate was so small that further tests had to be suspended. But from the examination made it would seem that the blue distillate obtained from this specimen of the oil of milfoil is not identical with that from the oil of chamonile. It is evidently closely related to the terpenes.

The quantities of the other distillates were too small for extended examination.

UNIVERSITY OF MAINE,
ORONO, MAINE.

NEW BOOKS.

THERMODYNAMIQUE ET CHEMIE. By P. DUHEM. 16 x 25 cm. pp. ix + 496. Paris: A. Hermann. 1902.

This is primarily a book on the phase rule, written for the chemist and not for the mathematical physicist. The first chapter deals with work and kinetic energy, the second with heat and internal energy. These two chapters are really introductory thermodynamics. We next have a chapter on heat effects and then one on chemical equilibrium. In the sixth chapter there is a discussion of the theorem of Carnot-Clausius, and of the thermodynamic potential. In the seventh chapter we find the phase rule outlined and ten chapters are devoted to the application to concrete cases. The general order is: multivariant systems, univariant systems, inversion points, displacement of equilibrium, systems with constant boiling- or melting-points, solid solutions, critical states, dissociation of gases. This comprehensive survey is followed by a chapter on apparent false equilibria and by one on false equilibria while the last two chapters are on systems with a non-uniform temperature and on chemical dynamics and explosions.

While one must regret that the arrangement of material is so haphazard, the way the material is treated is excellent and will

quicken interest in the subject. The treatment of indifferent points is especially complete and the reader will also get much profit from the chapters on solid solutions. The cream of the book, however, is to be found in the part on false equilibria and that in spite of one serious blemish. A number of experiments on false equilibria have been made in Duhem's laboratory or under his guidance and most interesting results have been obtained. These results have, however been called in question by Bodenstein who asserts that experimental error and a belief in the theory have led Duhem's scholars astray. This charge has never been met and there is no reference to Bodenstein in the book. This leaves matters in a most unfortunate position. The work of Pélabon, Hélier and others is very important, if correct, but not so important otherwise. As matters now stand, many chemists believe that there are reactions which do not start at a given temperature but there are very few who believe that a reaction runs part way and then stops short of a true equilibrium. Duhem's conception of "chemical friction" is a very valuable one, even though the experimental data are not above suspicion. Roloff's work on the cryohydrates appears to have been overlooked.

WILDER D. BANCROFT.

REFRIGERATION, COLD STORAGE, AND ICE-MAKING. By A. J. WALLIS-TAYLOR, C.E. London: Lockwood & Son; New York. D. Van Nostrand Co. Price, $4.50 net.

This practical treatise on the art and science of refrigeration is based on and embodies to a large extent the personal experience of the author. English methods and processes are most fully described. The whole subject is handled in a capable manner and the treatise will be found of service to teacher and student, and mainly to the technical engineer and those actually engaged in the various industries using refrigeration. The chemistry of refrigeration is only very superficially mentioned.

In an interesting table of the principal freezing mixtures, the author gives the reduction of temperature for a mixture of snow 3 to potassium 4 (?) as the maximum, 32° F. to —51° F. The lowest temperature obtainable by such mixtures is for snow 8 to dilute sulphuric acid 10 from —68° to —91° F., the materials themselves having been previously cooled. The subject-matter is classified under five principal heads:

I. The chemical processes, wherein the more or less rapid dissolution or liquefaction of solids is used to abstract heat.

II. The vacuum systems, wherein the abstraction of heat is produced by a partial evaporation of the substance, with the use of mechanical devices, such as pumps, etc.

III. The compression processes, wherein the abstraction of heat is effected by mechanical compression and the cooling of a separate agent, more or less volatile.

IV. The absorption system, wherein the abstraction is indirect, effected by direct heat on a separate agent, more or less volatile, which enters into solution with a liquid.

V. The cold air methods, wherein air or gases are compressed and cooled, and expansion takes place while doing work, an application of heat to ultimately produce cold.

The first ten chapters of the treatise, some 200 pages, are devoted to the description of these processes, and the other eleven chapters, 300 pages, being taken up with the application of these processes to refrigeration, classed under the following chapters: Cocks, Valves, Pipe-Joints and Unions; Refrigeration and Cold Storage; Marine Refrigeration; Ice-Making; The Management and Testing of Refrigeration Machinery; Cost of Working; Production of Very Low Temperatures. The sub-division of the chapter on Manufacturing, Industrial and Constructional Applications gives a very good idea of the whole character of this treatise; *viz.*, chocolate manufacture, breweries, paraffin works, artificial butter manufactories, dairies, dynamite factories, manufactories of photographic accessories, wine growers' and wine merchants' establishments, distilleries, sugar factories and refineries, chemical works, India rubber works, glue works, tea factories, and others, also manufacturing and industrial applications, tunnelling, sinking shafts, laying foundations, etc.

The book is profusely illustrated with some 300 wood cuts descriptive of processes and plants. The table of contents and index are complete. An appendix of useful tables and memoranda, and list of illustrations will be found of service. The book is comparatively free from errors. The use of the metric system in place of English weights and measures, and of the centigrade scale in place of the Fahrenheit, would be an improvement. The author has made free use of the literature on the subject, inclusive of

1901, relying for his American data on this completely. Full credit is given to others. The reluctance must be commended with which the author abstains from giving undue or special credit to any special process or machinery, thereby advertising same.

The treatise can be recommended as a useful and up-to-date description of the processes of refrigeration and their application to the arts. EDWARD GUDEMAN.

MODERN CHEMISTRY, WITH ITS PRACTICAL APPLICATIONS. BY FREDUS N. PETERS, A.M., Instructor in Chemistry in Central High School, Kansas City, Mo. New York: Maynard, Merrill & Co. 1901.

This text-book is intended to be used in secondary schools. As stated in the preface the author has endeavored to avoid giving too great a number of facts, to omit what can never be of interest or value to beginners and has tried to show, wherever possible, the practical applications of the science to every-day life and has emphasized industrial and commercial processes. At the same time the fundamental principles of the science have not been forgotten and due attention has been given to these.

On the whole the author has succeeded very well and this book is much superior to many that are now in use. After two introductory chapters, one on chemical and physical changes and the other on valence, which it would have been better to put later or omit altogether, he begins with water and then takes up hydrogen and oxygen. This is followed by nitrogen, the atmosphere, the halogen elements and carbon and a few of its simpler compounds. Then follows a chapter on the laws of definite and multiple proportions and combining weights. Sulphur, silicon and phosphorus are then considered after which a chapter is given up to Avogadro's law and atomic weights. Before considering the metals a very brief mention is made of the periodic law. The subjects are everywhere treated very briefly and concisely and the references to commercial processes are very elementary. The appendix contains directions for the qualitative analysis of simple substances.

There are a few errors which no doubt will be corrected in the next edition. Thus for example on page 147 the name ethane is given to olefiant gas. On page 224 plaster of Paris is referred to as anhydrous calcium sulphate. On page 226 the statement is made that the hardness of water is either "temporary or perma-

nent according as it can be removed by boiling or adding ammonia or not at all." It would have been well in this connection to have explained to the student how permanent hardness can be removed. On page 236 the explosive copper acetylide is given the formula CuC_2 instead of Cu_2C_2. The cut on page 290 should be omitted.

Taken as a whole the book is to be commended, and it will undoubtedly find an extended use in high schools and academies.

EDWARD H. KEISER.

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STUDIES IN DENITRIFICATION.

BY E. B. VOORHEES.

Received April 26, 1902.

PART I.

SINCE the beginning of these experiments in the early summer of 1898, many contributions have been made toward the better understanding of the various problems of plant nutrition. Among these, the nitrogen question has been receiving the attention of many investigators, and it has been examined from the different standpoints of the soil chemist, the soil physicist, and the soil bacteriologist. Much time and ingenuity have been devoted to the clearing-up of that phase of the nitrogen question known as "denitrification"—the destruction of the nitrates and the setting free of gaseous nitrogen. That deoxidation of combined nitrogen is liable to take place, and actually does take place in anaerobic fermentation, has been known for years, but the question assumed more than a mere scientific interest, since the emphatic declaration of Wagner[1] that applications of cow or horse manure to the soil are often not only unprofitable, but harmful; that, when applied together with the nitrates, they cause, by virtue of the micro-organisms contained in them, the destruction of the nitrates.

More than that, the baneful effects do not stop here, for the nitrates as they are gradually formed from the organic matter of the soil are also attacked by the denitrifying bacteria, and their nitrogen is set free. In a word, then, the animal manure applied is not only useless of itself, but is harmful because of its destructive effects on the oxidized nitrogen derived from other sources.

It is quite apparent that the interests involved are of great moment, that Wagner's theory if it be borne out by practical experience vitally concerns the man of science, the practical farmer, and the world at large. It was in the hope of contributing something to the knowledge of the subject that these experiments were planned. The scope of the work included the study of:

I. The composition of the solid and liquid portions of cow manure, fresh.

II. The composition of the solid and of the solid and liquid portions of cow manure, leached.

III. The availability of the nitrogen in the solid and in the solid and liquid portions of cow manure, fresh.

IV. The availability of the nitrogen in the solid and in the solid and liquid portions of cow manure, leached.

V. The relative availability of the nitrogen in the form of nitrate, of ammonia and of organic matter in dried blood.

VI. The effect of the use of the solid and of the solid and liquid portions of cow manure, fresh and leached, with nitrogen in the form of nitrate, of ammonia, and of organic matter.

DESCRIPTION OF THE EXPERIMENTAL PLANT.

In order that the conditions of the experiment might conform as nearly as possible to those in actual practice, what is known as the "cylinder method" was adopted.

The cylinders were made of galvanized iron, 23.5 inches in diameter and 4 feet long, and were painted inside and out, to retard corrosion. The area of soil surface thus exposed was, therefore, 3 square feet, and its depth was such that the roots of the crop would be practically prevented from obtaining food other than that contained within the cylinders. In order that the conditions for each cylinder might be uniform, the surface soil was first removed entirely, and the subsoil, a mixture of clay and sand,

which was taken from the holes, was thoroughly mixed. The same weight of subsoil was then placed in each one, and thoroughly packed and brought to a uniform height, so as to permit of the addition of 8 inches of surface soil; 120 cylinders were used, divided into two groups of 60 each. Thus in each group there were 20 series of three each, A, B and C, enabling a triplication of crops in each case.

DIAGRAM OF EXPERIMENT.

Series.	A.	B.	C.
1. Check	O	O	O
2. Minerals	O	O	O
3. Manure, solid, fresh	O	O	O
4. Manure, solid and liquid, fresh	O	O	O
5. Manure, solid, leached	O	O	O
6. Manure, solid and liquid, leached	O	O	O
7. Nitrate, 5 grams	O	O	O
8. Nitrate, 10 grams	O	O	O
9. Manure, solid, fresh ; nitrate, 5 grams	O	O	O
10. Manure, solid, fresh ; nitrate, 10 grams	O	O	O
11. Manure, solid and liquid, fresh ; nitrate, 5 grams	O	O	O
12. Manure, solid and liquid, fresh ; nitrate, 10 grams	O	O	O
13. Manure, solid, leached ; nitrate, 5 grams	O	O	O
14. Manure, solid, leached; nitrate, 10 grams	O	O	O
15. Manure, solid and liquid, leached; nitrate, 5 grams	O	O	O
16. Manure, solid and liquid, leached ; nitrate, 10 grams	O	O	O
17. Ammonium sulphate	O	O	O
18. Dried blood	O	O	O
19. Manure, solid, leached ; ammonium sulphate	O	O	O
20. Manure, solid, leached ; dried blood	O	O	O

SURFACE SOIL.

The surface soil for each group was selected to conform to two general standards—first, a medium clay, suitable for the cereals and grass crops, and second, a prepared sandy loam, suitable for

the various market-garden crops. The medium clay loam was obtained in the neighborhood of the Station from a field in which no crops had been grown for twenty years or more, and upon which no manure had been applied within the knowledge of those familiar with the land for a longer time. It was practically barren. The soil, however, was sifted, thus removing all stones and large lumps, as well as practically all vegetable matter. It was thoroughly mixed and a definite and equal weight placed to the depth of 8 inches upon the subsoil in each cylinder constituting Group I. The sandy loam was prepared by adding to the medium clay soil, already described, one-half its weight of sand, also obtained in the neighborhood, free from organic matter and practically free from any available mineral substances.

The soils for both cylinders were mixed with sufficient lime to supply any needed requirement, as well as to neutralize acidity, and, with the exception of Series 1, all of the cylinders received a uniform application of the minerals in the form of acid phosphate and muriate of potash, equivalent to 50 pounds of phosphoric acid and 75 pounds of actual potash per acre, which was believed to be sufficient to meet needed requirements. For the manures, the applications were greater than is usually the case in practice, but not so great as to be impracticable. The largest application would be equivalent to about 20 tons to the acre, an amount often exceeded in practice.

In the case of the nitrogen in artificial forms, the nitrates only were applied in two different quantities, in the one case 5 grams per cylinder, equivalent to 160 pounds per acre, which may be regarded as medium, and in the second, 10 grams per cylinder, equivalent to 320 pounds per acre, or a large application. This was done in order that the effect of denitrification, if any, might be more fully studied. In the case of the ammonia and blood, an amount of nitrogen equivalent to that in the larger quantities of nitrate was applied. Similar applications were made in the following years.

At the end of each growing season, determinations were made of the actual dry matter in the different crops, of the percentage of nitrogen contained in them, of the gain in nitrogen due to the materials added, and of the percentage of the applied nitrogen recovered.

The results obtained are definite and clearly point in one direction, in so far as the question of denitrification is concerned, and are in accord with those of other investigators. The experimental data accumulated during the years 1898, 1899, and 1900 will be presented in the second part of this paper.

As the work progressed and the accumulated material was studied, other questions presented themselves. They concern the movement of the plant-food in the soil and in the plant, the relation of the mineral salts to the organic matter, the influence of rainfall, the rapidity of nitrification, etc. While still following the main lines of research, as indicated, the other points have been examined in so far as was practicable, and deductions drawn where the experimental data at hand warranted it. Obviously the many factors that determine the yield of crop are so closely related to one another, that a true understanding of the subject can only come with the careful study of the soil from more than one standpoint. As a recent bulletin aptly expresses it:[2] "Our first object is to determine the *controlling* factor of fertility, whether and when this factor is physical, depending upon the color, texture, or structure of the soil; climatological, depending upon temperature, sunshine, and rainfall; chemical, depending upon the absolute chemical composition, or upon a definite minimum solubility of the soil's constituents", or, we might add, bacteriological, depending upon the activity of soil organisms.

That the latter is not the least important is attested by the numerous researches on their relation to the nitrogen question, both in its constructive and destructive phases. According to Stoklasa,[3] "the assimilation of the nitrogen of the air by bacteria forms one of the most important problems of modern biological research." On the one hand, we have the symbiotic life of the *B. radicicola* with the plants of the leguminous family resulting in the fixation of atmospheric nitrogen; on the other hand, we have organisms like *Clostridium Pasteurianum*, which, as Winogradsky has shown, can assimilate atmospheric nitrogen independently, or Caron's *Bacillus Ellenbachii*, which Stoklasa claims can also assimilate atmospheric nitrogen. These and others probably constantly work to preserve and increase our stock of combined nitrogen in the soil,—they are the constructive agents. At the same time there exist in the soil, and in decaying vegetable matter, numerous

micro-organisms that have the power under the proper conditions to break up certain nitrogen compounds, and in this process much or all of the nitrogen is returned to the atmosphere whence it originally came, in the gaseous state. These latter organisms are the destructive agents. It is their activity that concerns the subject of our inquiry more directly, and a brief review of the more important work along these lines will help us to understand better the experimental data submitted in this paper.

As far back as 1867, Froehde had observed[4] that the reduction of nitrates takes place, at times, when they are in contact with certain organic substances. There appeared to be a considerable number of the latter possessing such reducing properties. From that early observation to our present knowledge of the specific micro-organisms causing, under given conditions, the destruction of nitrates, the study of the subject, though gradual, was decidedly irregular. It was only within the last five or six years that a careful and systematic examination of the question enabled us to gain a more definite conception of the processes of denitrification. For all that, there is much that is yet obscure, and much that calls for further study. The latter is particularly true of the denitrification processes as they appear in practical agriculture, since, as has been pointed out repeatedly, the conclusions obtained from laboratory experiments are not always applicable to actual practice, creating as they do abnormal conditions not encountered in the field. As with nitrification, the earlier investigators attempted to explain denitrification by purely chemical reactions, and to the French chemists largely belongs the credit for being the first to point out to us the probable bacterial character of the denitrification processes. However, some years before that, Schoenbein[5] had noticed that nitrates are reduced to nitrites by fungi, and that the presence of nitrites in drinking water might indicate that it contains micro-organisms. Dr. Angus Smith, in 1867, had also noticed[6] that a reduction of nitrates with the evaporation of free nitrogen takes place in the decomposition of sewage.

The work done since then, and leading up to the more detailed recent studies, will be briefly reviewed here. Meusel[7] observed the transformation of nitrates into nitrites in drinking-water, and attributed the formation of nitrites to bacteria. Chabrier states[8] that all soils contain nitrous acid, that in dry weather nitrates

accumulate at the surface, and that nitrites occur in larger quantity in the lower layers of the soil. In another place[9] he finds that there is a small loss of nitrogen (liberated as gaseous nitrogen) in nitrification. This latter fact was also observed somewhat later by Boussingault[10] and later by Pickard[11] and subsequently by Godlewski.[12] Jeannel[13] found that when in contact with humus; dead leaves and straw, nitrates are reduced to nitrites; and Schloesing[14] showed that in a large bottle, whose atmosphere was kept free from oxygen, potassium nitrate was reduced to ammonia, and, also, some of the combined nitrogen was set free. Boname,[15] a year later, also came to the conclusion that nitrates are reduced in an atmosphere free from oxygen To Schloesing,[16] also, belongs the credit of having established the fact that nitrogen is set free in the putrefactive decomposition of urine and in the lactic fermentation of sugar in the presence of potassium nitrate.

Pesci[17] noted that nitrates are reduced to nitrites when the action is allowed to go on under water, and E. W. Davy[18] observed that an excess of animal matter in solution retards nitrification. Hüfner,[19] on the other hand, decided that no gaseous nitrogen is set free in the decay of organic substances.

Deherain and Maquenne[20] had also observed the reduction of nitrates. They attributed this action to anaerobic ferments, and showed that the gases set free contained besides carbon dioxide, also free nitrogen and nitrous oxide. About the same time Gayon and Dupetit[21] studied the reduction of nitrates in the soil. They describe an anaerobic "ferment" capable of reducing nitrates rapidly. In this process, gaseous nitrogen is set free. They also found that the ferments need organic matter for their development, that part of the organic nitrogen is transformed into ammonia, and, perhaps, also into amido derivatives of the organic substance. Heraeus,[22] too, had observed the reduction of nitrates to nitrites and ammonia by bacteria, and Springer[23] studied what he called a "ferment," rod-shaped, rounded at the ends, and capable of reducing nitrates.

In 1886, Gayon and Dupetit[24] isolated two organisms, *B. denitrificans I* and *B. denitrificans II,* capable of reducing nitrates with the evolution of gaseous nitrogen. Besides these they encountered a number of bacteria that could reduce nitrates to nitrites. According to the composition of the nutritive medium

the nitrogen of the nitrates may be set free as such, or mixed with nitrous oxide. The oxygen of the nitrates not combined with the nitrogen of the nitrous oxide, unites with the carbon of the organic matter, giving carbon dioxide, which dissolves for the most part forming bicarbonate of potassium (KNO_3 being used). The culture medium containing 10 grams of potassium nitrate begins to ferment on the addition of some soil. The authors think that the decomposition of nitrates by *B. denitrificans* is not a true fermentation, nor a secondary phenomenon, but a "combustion of the organic matter by the nitric oxygen with the liberation of much heat; it is a type of fermentation that can take place only with the simultaneous concurrence of several chemical reactions." Kellner and Yoskii[25] found that although losses of nitrogen occur in the decay of nitrogenous organic matter, yet the losses are slight, even after the decay has progressed for a long time. Ehrenberg[26] in a series of exhaustive experiments showed that "neither in the presence nor absence of free oxygen, neither in solution nor in slightly moistened decaying masses permeable to gases, is elementary nitrogen set free through the agency of micro-organisms." Tacke[27] reaches a similar conclusion, while Immendorf[28] stated distinctly that according to his experiments the setting free of nitrogen from decaying organic matter is not a purely chemical process, but is effected with the aid of micro-organisms. It will be seen from this that while there were still adherents of the chemical theory in Germany, the belief was beginning to prevail that the destruction of nitrates is due to bacteria. Two years later Tacke[29] admits that Berthelot was right when he claimed that there are nitrogen-fixing bacteria in the soil, and adds that there are also present in the soil organisms that set free nitrogen from its compounds.

Holdefleiss[30] was led to believe that even in yard manure constantly compacted by animals, and with the oxygen thus excluded, the nitrification processes take place to some extent. Hence, the greatest loss through the formation of free nitrogen takes place in the manure pile, and not in the stable. By compacting the manure, the nitrification processes can be limited, and we must depend on mechanical treatment to delay nitrification until the manure reaches the soil. Of course, in preventing nitrification in the manure pile,

the losses of free nitrogen due to denitrification are largely prevented.

Leme[31] found that the addition of large quantities of fresh manure, not only stops nitrification, but that there is at first a reduction of nitrates to nitrites, and of the latter to ammonia. Breal[32] announced that many substances of organic origin, and especially straw, are the carriers of denitrifying organisms. Obviously the discovery is of far-reaching importance. Since these organisms are carried to the manure in the litter, and later are plowed in the soil with the manure, it becomes interesting to determine to what extent denitrification takes place, either in the manure pile or in the soil. In order that denitrification might take place, it is essential that nitrates be present, and we must assume that where no nitrates are applied as such, nitrification must first take place that denitrification might follow. E. W. Davy,[33] Leme,[34] Pickard,[35] Lipman,[36] and others have shown that large quantities of organic matter either retard or entirely stop nitrification, and for that reason the losses of nitrogen from fresh manure due to the destruction of nitrates cannot be great. On the other hand, losses of nitrogen may take place in other ways, and there is much evidence that confirms this view.

König[37] in his prize essay stated that "the losses of nitrogen from manure due to the volatilization of ammonia appear to be slight," and he is inclined to think that the greater losses are due to the liberation of elementary nitrogen. Immendorf,[38] on the other hand, comes to the conclusion that the chief cause of the loss of combined nitrogen in manure with the usual treatment may be attributed to the volatilization of ammonia, and finds that the formation of elementary nitrogen influences these losses only to a limited extent. Burri, Herfeldt and Stutzer[39] carried out some experimental work to decide as to the causes that lead to losses of nitrogen in decaying organic substances, especially in dung and liquid. They are led to believe that where denitrification takes place it is preceded by nitrification. Hence they conclude that "in the decay of nitrogenous organic substances, there is no setting free of elementary nitrogen as long as the activity of the nitrifying organisms in the decaying substance is suppressed." On the other hand, they believe that a considerable evolution of free nitrogen may take place when nitrates are added to dung or

liquid manure, or when opportunity is given to the nitrifying organisms for active development. The splitting off of free nitrogen may be caused by the reduction of nitrates, or by the action of nitrous acid or ammonia or amines. The authors point out later that denitrification is rather due to living organisms than to purely chemical reactions, as Ehrenberg[40] assumes; nitrification, they think, may run to completion without the evolution of free nitrogen; such evolution is more likely to take place in the decaying mass when the supply of oxygen is limited. In such cases the oxygen of the nitrates is utilized and the nitrogen is set free.[41] Since in the fresh manure scarcely any nitrification takes place, the denitrification cannot be considerable. In another communication the same authors suggest that the object of a rational method of conservation should not only consist in preventing the volatilization of ammonia, but also in controlling the course of fermentation, so as to favor the development of bacteria that transform organic nitrogen into ammonium carbonate.

Following the example of Gayon and Dupetit, Burri and Stutzer were led to attempt the isolation of denitrifying organisms. The work appeared the more desirable in view of Breal's[42] discovery already alluded to, and of a communication from Wagner that nitrate of soda yielded inadequate returns when used together with horse manure. In communicating the results of their experiments[43] they call attention to the fact that there are but a limited number of organisms capable of oxidizing nitrates, while of those possessing the power of reduction (deoxidation) the number is great. Of these, however, the greater part can only reduce nitrates to nitrites and the bacteria capable of reducing nitrates to ammonia, or of setting nitrogen free, are not very numerous. Of the work not already referred to, they mention that of Deherain and Maquenne[44] who observed that in the gases set free in denitrification there is contained besides nitrogen, also carbon dioxide and hydrogen. Also the work of Giltay and Aberson[45] is mentioned. The latter describe a bacillus capable of destroying large quantities of nitrate with the evolution of free nitrogen. Burri and Stutzer finally succeeded in isolating two organisms capable of reducing nitrates completely, which they named *B. denitrificans I* and *B. denitrificans II.* Their conclusions[46] may be summed up as follows: "When oxygen is completely excluded *B. denitrificans I,* together

with *B. coli*, does not cause the evolution of free nitrogen in culture solutions containing nitrate, but most of the nitrate nitrogen is reduced to nitrite nitrogen. With a limited supply of oxygen, *B. denitrificans I* can develop to such an extent as to be able, together with *B. coli*, to cause the fermentation of nitrate with the evolution of free nitrogen. When once started the fermentation takes its usual rapid course. *B. denitrificans I* uses in this case some of the oxygen derived from the nitrates. With a liberal supply of air *B. denitrificans I*, together with *B. coli*, causes the destruction of nitrites in the normal way. With the complete exclusion of air *B. denitrificans II*, to cause the fermentation of nitrates, is diminished or entirely suppressed.

According to Marchal[47] the behavior of *B. mycoides* in nutritive solutions containing nitrates is rather striking. When inoculated into a solution containing glucose and about 2 grams of potassium nitrate per liter, nitrites and ammonia could be detected in a few days, and in fifteen days ammonia alone. It appears thus that the same organisms may exert either an oxidizing or reducing action. Both processes are intimately connected with the respiration of the organism. In one case albuminoids are normally oxidized with the aid of atmospheric oxygen; in the other, the intramolecular respiration leads to a utilization of the nitrate oxygen to oxidize the sugar.

Attempts to isolate denitrifying organisms were also made by Schirokikh.[48] He was successful in obtaining a pure culture of an organism capable of destroying nitrates. He describes it as a bacillus with rounded ends, having no vacuoles, and one and a half to twice as long as it is wide. It is motile, though not as markedly as, for instance, *B. pyocyaneus.*

A further study of the denitrifying organisms isolated by Burri and Stutzer[49] is contributed by Stutzer and Maul[50]. The authors finally come to the conclusion that *B. denitrificans I*, together with *B. coli*, destroys nitrates in a flask that is merely stoppered, but when air is passed through the liquid in the flask, denitrification is not as active. Also Ampola and Gatino[51] isolated a denitrifying organism which they named *B. denitrificans agilis*. They found that it is capable of destroying nitrates rapidly. In examining the gases evolved they found them to consist of nitrogen and carbon dioxide, the latter being present to the extent of 15 per cent. In

searching for practical means to diminish denitrification in manure, the same authors[52] decided that peat prevents denitrification by virtue of the acidity it imparts to the manure, but when the manure again becomes alkaline denitrification takes place.

S. A. Sewerin[53] isolated thirty-two different organisms from horse manure, and studied twenty-nine of these. In one case strong foaming was noticed, and it was found that there were at least two species capable of reducing nitrates completely. Further study showed that there were also nine species capable of reducing nitrates to nitrites, eighteen species being indifferent. By diluting the nitrate solution to 0.1 per cent., two more showed complete reduction, and still further dilution to 0.05 per cent. showed four more organisms capable of complete reduction, in all eight species. It appears also that proportionately larger quantities of potassium nitrate than of sodium nitrate are reduced in a given time, and 0.6 per cent. of sodium nitrate appears to be the limit of reduction. The author also finds that the stirring of the soil and greater aeration tend to diminish denitrification.

His studies of *B. denitrificans II* led Hjalmar Jensen[54] to believe that it can be grown as an aerobe. He finds a certain relation between the nitrate destroyed and the carbon compounds used. No denitrification takes place without a source of carbon being supplied.[55]

P. P. Deherain[56] confirms Breal's claim that there are denitrifying bacteria on straw, and Wagner's that these organisms are found in animal excreta. He finds that they occur in cultivated soils; that the nitrogen set free by them is accompanied by carbon dioxide, and often by nitrous oxide; that the nitrogen used by the organisms to build their tissues are comparatively small; they utilize only the oxygen of the nitrate and more readily exercise their reducing action in a closed space. When ordinary quantities of manure are applied nitrification rather than denitrification takes place. It is hardly necessary to treat the manure with sulphuric acid to destroy the denitrifying organisms.

It has been noted above that of denitrifying, or nitrate-destroying organisms, a large number are known at the present day, and there is no doubt that when a more thorough study is made of the subject many more will be added to the list. Thus Stoklasa[57] enumerates the following bacteria as capable of causing the fer-

mentation of nitrates in the presence of organic acids, or of pentoses and hexoses: *B. humosus, B. fluorescens liquefaciens, B. pyocyaneus, B. denitrificans, B. coli communis, B. Stutzeri,* and many others that have been studied less carefully. As it is to be expected, these organisms do not possess the power of denitrification in an equal degree. The author just referred to says that the analysis of the gas produced by *B. Hartlebii* showed 70 to 96 per cent. of nitrate nitrogen set free, the rest having been transformed into organic nitrogen. Furthermore, the destructive fermentation of nitrates depends to a great extent on the character of the organic acids in the nutritive medium, some being much better adapted than others to furnish the necessary energy for the breaking-down of the nitrates. Stoklasa also claims that most of the denitrifying bacteria can cause no reduction of nitrates in media where chemically pure *d*-fructose and *d*-galactose are present. The nitrate, he believes, is first reduced to ammonia, and that is oxidized with the liberation of free nitrogen. However, not all of the ammonia is thus oxidized, for a part of its nitrogen is transformed into the organic form, a fact that was long ago noticed by Schloesing[58].

An interesting study of several manure bacteria and of the products of their activity is contributed by T. Severin.[59] Of the several organisms that he isolated from manure, some seem to differ materially from the others. Thus *B. pyocyaneus,* and what he calls *B. No. 2,* will not produce carbon dioxide and ammonia from solid manure alone, but will attack it when it is mixed with liquid manure. On the other hand, one organism which the author designates as *No. 1* seems to be more active in the absence of urine. This fact is significant in that it introduces a new factor in the study of the relative value of solid and of solid and liquid manure in plant nutrition.

Some of the accumulated facts bearing on the conditions most suitable for the growth and development of the denitrifying bacteria we owe to Stutzer. In a recent article[60] he claims that denitrification in nutritive solutions is not favored by glucose, but is promoted by the presence of salts of organic acids, like potassium lactate or potassium citrate.

Turning to the more practical side of the denitrification question, we find that much thought has been given to it. Some years

ago the experimental data at hand were so contradictory, and the points to be cleared up so numerous, that Pfeiffer was led to say: "There is scarcely another field of research in agricultural chemistry in which we encounter contradictions as numerous, and as fully unexplained." In order to clear up these contradictions and to throw more light on the doubtful results, the German Agricultural Association called for a united effort on the part of the German experiment stations, offering at the same time to place the necessary means at their disposal.[61] The call was answered and the work undertaken by the experiment stations of Augsburg, Darmstadt, Jena and Rostock, and later on by the Bonn and Göttingen stations. The investigation was to answer two general questions:

1. How are the great losses of nitrogen that take place in the decay of organic substances to be explained? To what extent is the nitrogen liberated in the elementary state, and to what extent as ammonia, and how does the liberation of the first take place?

2. What means do we possess of checking these losses, and how does the material thus employed act?

The publication of the results was to be delayed until the existing uncertainty was cleared up. Since such was far from being the case in 1896, it was decided to publish the results already received at that time, for they contained much that is valuable, and in many respects conclusive. In accordance with this, there appeared in the *Landwirtschaftlichen Versuchs-Stationen*[62] the reports of B. E. Dietzel (Augsburg), of Th. Pfeiffer, E. Franke, C. Götze, and H. Thurmann (Jena), and of J. Aeby, R. Dorsch, Dr. Matz and P. Wagner (Darmstadt). The combined reports make a very valuable contribution to the subject of denitrification, and will well repay a careful study to all who are interested in the nitrogen question.

The Jena and Darmstadt stations have reached similar conclusions in regard to certain phenomena. The experiments of both indicate that with a limited supply of air in the manure, the losses of elementary nitrogen and of organic substance are not very extensive. It might be added here that the results obtained at the Darmstadt station[62a] indicate that "solid excreta and straw lose their nitrogen so very slowly, that no conservation materials are

needed. It is only the nitrogen of urine that requires conservation."

Pagnoul[64] had found that horse manure, especially in the presence of starch, tends to cause the disappearance of nitrates, but at 30° with a sufficient supply of oxygen and water, there is no loss of free nitrogen, but the conversion of nitrate into organic combinations. It should be added here, perhaps, that the same investigator had some years earlier[65] declared that ordinary quantities of horse manure do not cause denitrification in the soil.

Also Ragoyski[66] found that lime largely prevents the loss of nitrogen. It is very likely that the increase in albuminoid nitrogen was due to the activity of bacteria, for also Street[67] and others have found this to be the case; but as to the availability of the organic nitrogen thus formed, there is a considerable difference of opinion. Nobbe and Hiltner[68] state definitely that the organic nitrogen produced by soil bacteria is not available, at least not immediately available, to the growing crop.

Pfeiffer, Franke, Lemmermann, and Schilbach[69] studied the availability of the nitrogen in different nitrogenous materials in both pot and field experiments. The substances used were sodium nitrate, ammonium sulphate, ground horn, dried blood, meat and bone, and barnyard manure, both treated and untreated.

It would not be out of place here to examine a certain statement of the authors that had a direct bearing on facts brought out in our own experimental work. They attempt to account for the high nitrogen content of plants grown on a soil poor in nitrogen.[70] Quoting Maercker's explanation,[71] "that on a soil very poor in nitrogen, the plants starving for want of nitrogen do not pass their period of infancy; on account of their lack of nitrogen they are not able to form sufficient amounts of carbohydrates, and these result in abnormal plants, which die before they mature, and, therefore, are rich in nitrogen, while containing but a small amount of dry matter." The authors criticize this statement and point out that there must have been some other controlling factor, for with a plentiful supply of the other plant food constituents, there should result a mass of plant food substances of a normal composition. A comparison of Series 1 and 2 in our experiments will show that they are right in this respect.

In an article entitled[72] "The Cause and Significance of the De-

composition of Nitrates in the Soil," Krüger and Schneidewind report the results of their experiments. The work was undertaken in order to solve the following problems: (*a*) Does the loosening of the soil caused by applications of manure have anything to do with the diminution in yield? (*b*) Is it caused by the addition of organisms that destroy nitrates? (*c*) Is it caused by the addition of substances which favor the development of the nitrate-destroying organisms, and thereby favor denitrification?

The investigation included both plot and field experiments, 6 kilos of soil being used in the former. They find that there was denitrification in the plots, there being in every case a smaller yield over the nitrate alone when together with the latter fresh manure is used, and that with varying quantities of nitrates.

The authors express the belief that while the denitrification processes in the field are not as extensive as they are in the cylinders, yet even in field operations the denitrification processes are of considerable significance. The decomposition of nitrates in the field is not usually noticeable, because the nitrification processes here are more intense than they are in the cylinders, and hence denitrification is less marked. Denitrification is also masked on the addition to the field of barnyard manure, because there is more soluble nitrogen added by the latter to the soil than is destroyed by the denitrifying bacteria. "A direct conclusion as to the extent of denitrification in practice can only be obtained by determining the action of liquid manure, or of nitrate for itself on the one hand, and on the other hand the action of either when used together with solid excreta and straw."

Pfeiffer and Lemmermann[73] do not agree with Krüger and Schneidewind in their claim that denitrification caused by manure is due to the organic matter it adds to the soil, rather than to the bacteria contained in it.

Maercker had pointed out[74] that in the course of sterilization of manure, certain substances are formed that are injurious to plant life. It follows, if this be true, that a comparison in vegetation experiments of sterilized and unsterilized manure would not bring out the actual relations. To avoid this difficulty, Pfeiffer and Lemmermann sterilized both lots, and then inoculated one of them with a pure culture of *B. denitrificans II*, given to them by Dr. Kunnemann. They find that there is an increase in the soil nitro-

gen of all the cylinders on which no nitrogen had been applied, and are inclined to ascribe the cause of it to nitrogen-fixing bacteria. This view is confirmed by the experience of Aeby,[75] of Schneidewind,[76] and of Richter.[77] The latter sums up his conclusions as follows: (1) The several unsterilized vessels to which no nitrogen had been added show an increase in nitrogen. The gain is slight in the first crop, but increases later. (2) In all cases where nitrogen is applied, there is a loss of soil nitrogen. Hence the increase of nitrogen in the soil takes place only when the latter is poor in assimilable nitrogen.

Pfeiffer and Lemmermann are also inclined to think that since a part of the nitrate nitrogen is changed into the organic form, and is later utilized by the plant, it is manifestly unjust to decide on its relative availability from short vegetation experiments. Finally they conclude that there are several factors responsible for the so-called denitrification process. There are at least three such factors, and namely:

1. Direct injury to the growing plants by larger quantities of organic substance.

2. Fixation of soluble nitrogen by the increased activity of different organisms.

3. Denitrification proper.

It is still to be learned which one of these factors plays the most important part, economically and how we are to modify and influence such activity.

From his more recent experiments[78] Rogoyski concludes that there is a denitrification of nitrates in the presence of large amounts of manure, the nitrogen being set free in the elementary state, while a part of it transformed into organic combinations. Similar changes occur when soil containing large quantities of manure or straw is mixed with urine or a solution of ammonia salts. The nitrogen thus fixed appears to be readily nitrifiable. When quantities used in practice were applied no denitrification took place, and the urine was nitrified. On the other hand, denitrification did take place when excessive quantities were applied.

The work of Wood[79] indicates that there was considerable denitrification when manure at the rate of 10 to 20 tons per acre was applied, together with nitrate. While there was some denitrification where well-rotted manure was used, the effects were more

striking in the case of fresh manure. Thus nitrate alone gave an increase of 9.5 bushels of grain per acre, while nitrate together with fresh manure gave practically no increase.

At present Höflich[80] is reporting studies in which he is trying to differentiate between denitrifying bacteria naturally occurring in soils, straw and manures.

The above represents a brief review of most of the recent research work on denitrification and the changes in manures. The fact that great losses of nitrogen take place when excessive amounts of manure are applied, and that, conversely no denitrification, or very little denitrification, takes place when ordinary quantities are applied, taken together with the experiments of Pfeiffer and Lemmermann to prove that much of the reduction in yield usually attributed to denitrification is really due to the injurious effect of large amounts of organic matter, indicate that there is a phase of the subject that needs very careful investigation.

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PART II.

The work carried on in our own laboratory[1] tends to confirm the claim of the European investigators. It shows clearly that nitrates when in contact with manure are destroyed by the organisms contained in the latter, that this destruction of nitrates is essentially a reducing process, that the larger portion is set free as gaseous nitrogen, and that a part of it is converted into ammonia, and part of it into insoluble organic nitrogen, not suited to supply the immediate nitrogen requirements of the growing crop. It shows, moreover, that other manurial substances, like acid phosphate, kainite, ammonium sulphate, etc., modify the transformation of the nitrate nitrogen. In interpreting these laboratory results, and in studying the conclusions drawn, it becomes necessary to determine their applicability to actual practice. The cylinder experiments whose plan and scope were presented in the first part of this paper are carried on under conditions approximately those in the field, and on a scale extensive enough to permit of conclusions and deductions of great practical importance. The use of fresh and of leached manure intended to answer still another question of direct concern to every farmer; and namely, what relative value they possess when used by themselves, or together with nitrogen salts, or with highly nitrogenous organic substances. The composition of the fresh manures, and of the leached manures, used in the experiment are shown in the accompanying table.

[1] John P. Street: N. J. Sta. Rep., 1899, p. 86, and Rep, 1900, p. 79.

TABLE I.

	Leached manures.		Fresh manures.	
	Solid. Per cent.	Solid and liquid. Per cent.	Solid. Per cent.	Solid and liquid. Per cent.
Water	77.043	78.614	85.794	85.074
Ash	3.176	3.005	1.831	2.645
Organic matter	19.781	18.381	12.375	12.281
Nitrogen (total)	0.431	0.498	0.293	0.463
Nitrogen, water-soluble	0.056	0.169	0.060	0.211
Nitrogen as nitrates			0.015	0.031
Nitrogen as ammonia		0.080	0.031	0.090
Nitrogen as soluble organic	0.056	0.089	0 014	0.090
Nitrogen as insoluble organic	0.375	0.329	0.233	0.252
Phosphoric acid	0.504	0.508	0.372	0.410
Potash	0.350	0.414	0.141	0.199

As already stated, a study not only of the relative effect of the constituent nitrogen in the various manures themselves, but also of its effect when used in connection with nitrogenous materials possessing a known rate of availability, was made the subject of the experiment, thus enabling a comparison of the relative availability of the nitrogen, as well as the denitrifying effect of the various manures.

Since the manure on the farm is so often exposed to the leaching action of rain before it is put on the field, it becomes apparent that the economic interests involved are of great moment.

In the tables presented in this paper, the attempt has been made to arrange logically the experimental data thus far obtained.

THE RESULTS OF THE OAT EXPERIMENT, 1900.

The accompanying table shows the actual dry matter in the different crops, the percentage of nitrogen contained in them, the gain in nitrogen due to materials added, and the percentage of the applied nitrogen recovered. In all cases, the net gains in the different series are derived by subtracting the average gain obtained on Series 2, upon which minerals only were applied, from the average gain for that particular series.

As in the crops of 1898 and 1899, there was a gain in weight of the dry matter of the crops to which nitrogenous materials were applied.

TABLE II.—RESULTS OF THE OAT EXPERIMENT.

Series.		Nitrogen applied.	Dry matter in crop.	Nitrogen in dry matter.	Nitrogen in crop.	Increase over check plot.	Per cent. of nitrogen recovered.	Average per cent. of nitrogen recovered.
		Grams.	Grams.	Per cent.	Grams.	Grams.		
1	A		81.8	1.397	1.143	...		
	B		82.6	1.313	1.085	..		
	C		84.8	1.293	1.096			
2	A		116.9	1.018	1.190			
	B		106.8	1.061	1.133	(1.152)		
	C		107.1	1.058	1.133			
3	A	4.05	154.0	1.061	1.634	0.482	11.90	
	B		155.3	1.108	1.721	0.569	14.05	10.81
	C		123.8	1.142	1.414	0.262	6.47	
4	A	3.98	232.4	1.143	2.656	1.504	37.78	
	B		208.3	1.069	2.227	1.075	27.01	30.60
	C		213.3	1.044	2.227	1.075	27.01	
5	A	3.99	128.5	1.145	1.471	0.319	7.99	
	B		121.7	1.121	1.364	0.212	5.31	7.38
	C		131.2	1.147	1.505	0.353	8.85	
6	A	4.04	193.4	1.096	2.120	0.968	23.96	
	B		193.7	1.067	2.067	0.915	22.65	22.06
	C		193.7	1.003	1.943	0.791	19.58	
7	A	0.78	158.0	1.163	1.838	0.686	87.95	...
	B		166.3	1.035	1.720	0.568	72.82	80.43
	C		174.7	1.019	1.780	0.628	80.51	
8	A	1.55	202.3	1.178	2.383	1.231	79.42	
	B		184.0	1.252	2.304	1.152	74.32	76.30
	C		198.4	1.168	2.317	1.165	75.16	
9	A	4.83	197.3	1.085	2.132	0.980	20.29	
	B		189.5	1.119	2.121	0.969	20.06	19.97
	C		199.2	1.052	2.096	0.944	19.55	
10	A	5.60	207.0	1.251	2.590	1.438	25.68	
	B		227.2	1.316	2.990	1.838	32.82	27.99
	C		232.9	1.107	2.578	1.426	25 46	
11	A	4.76	265.4	1.277	3.389	2.237	47.00	
	B		260.1	1.077	2.801	1.649	34.64	41.43
	C		269.0	1.183	3.182	2.030	42.65	
12	A	5.53	262.5	1.428	3.949	2.797	50.58	
	B		242.2	1.436	3.478	2.326	42.06	44.68
	C		285.9	1.204	3.442	2.290	41.41	

Series.		Nitrogen applied.	Dry matter in crop.	Nitrogen in dry matter.	Nitrogen in crop.	Increase over check plot.	Per cent. of nitrogen recovered.	Average per cent. of nitrogen recovered.
		Grams.	Grams.	Per cent.	Grams.	Grams.		
13	A	4.77	178.6	1.150	2.004	0.852	17.86	
	B		169.8	1.143	1.941	0.789	16.54	17.50
	C		178.5	1.129	2.015	0.863	18.09	
14	A	5.54	192.6	1.333	2.567	1.415	25.54	
	B		206.4	1.203	2.483	1.331	24.03	24.25
	C		196.4	1.241	2.437	1.285	23.19	
15	A	4.82	217.5	1.335	2.904	1.752	36.35	
	B		211.5	1.236	2.624	1.472	30.54	31.71
	C		217.0	1.158	2.513	1.361	28.24	
16	A	5.59	257.4	1.418	3.650	2.498	44.69	
	B		230.4	1.420	3.272	2.120	37.75	38.32
	C		214.1	1.387	2.970	1.818	32.52	
17	A	1.52	194.5	1.142	2.221	1.069	70.33	
	B	...	178.3	1.221	2.177	1.025	67.43	68.84
	C		191.2	1.149	2.197	1.045	68.75	
18	A	1.49	173.6	1.094	1.899	0.747	50.13	
	B		187.3	1.060	1.985	0.833	55.91	52.15
	C		175.4	1.085	1.903	0.751	60.40	
19	A	5.51	177.4	1.176	2.086	0.934	16.95	
	B		197.9	1.235	2.444	1.292	23.50	20.63
	C		201.8	1.156	2.333	1.181	21.43	
20	A	5.48	189.5	1.154	2.187	1.035	18.89	
	B		179.2	1.200	2.150	0.998	18.21	19.20
	C		198.7	1.145	2.275	1.123	20.49	

THE AVAILABILITY OF THE NITROGEN IN THE SOLID AND IN THE SOLID AND LIQUID PORTIONS OF FRESH MANURE.

In 1899, the problem was more complicated, because of the varying quantities of nitrogen applied in the manure.[1] Such was not the case, however, in the crop under consideration, for the amounts of nitrogen applied in the manure were practically uniform. In every case where manure was used, enough was applied to furnish nitrogen practically equivalent to 4 grams.

[1] Twenty-First Annual Report N. J. Expt. Sta.

1899.

Series 3, nitrogen applied = 3.32 grams.
Series 3, nitrogen applied = 5.25 grams.
Recovered in crop, 3- 8.3 per cent.
Recovered in crop, 4-40.2 per cent.

1900.

Nitrogen applied = 4.05 grams.
Nitrogen applied = 3.98 grams.
Recovered in crop, 3-10.81 per cent.
Recovered in crop, 4-30.60 per cent.

It appears, then, that in each case the recovery from the solid and liquid, combined, was greater than that from the solid manure alone. However, the relations are not quite the same, for in 1899 the recovery from the solid and liquid was nearly five times that from the solid alone, while in 1900, the recovery from the solid and liquid, combined, was not quite three times that from the solid alone. The fact that the comparative recovery was greater from the solid manure alone, indicates that the greater amounts of moisture rendered greater quantities available. As with the results of 1899, it is quite evident here that a large recovery may be expected from the soluble nitrogen in liquid manures.

The greater yield of dry matter over check (Series 2), was 31 per cent. for the solid, and 97.6 per cent. for the solid and liquid. The corresponding figures for 1899 were 35.9 per cent. and 228.8 per cent. This again indicates that with more rain the solid manure makes a better showing. It should be borne in mind, nevertheless, that the better showing for the solid and liquid manure in 1899 was due in a measure to the larger application of 5.25 grams, as against 3.98 grams in 1900.

THE AVAILABILITY OF THE NITROGEN IN THE SOLID AND IN THE SOLID AND LIQUID MANURE, LEACHED.

1899.

Nitrogen applied in leached manures, Series 5, 1.96 grams.
" " " " " " 6, 4.52 grams.
Recovered in crop..... " 5, 8.4 per cent.
" " " " 6, 13.8 per cent

1900.

Nitrogen applied in leached manures, Series 5, 3.99 grams.
" " " " " " 6, 4.04 grams.
Recovered in crop..... " 5, 7.38 per cent.
" " " " 6, 22.06 per cent.

The differences in recovery in the leached manures between the solid and the solid and liquid portions, are not as great as in the fresh manures. The recovery in the solid leached is proportionately somewhat less in 1900, but in the solid and liquid leached the recovery in 1900 is much greater than that in 1899. In the preceding year, however, the recovery in the leached manures is less than the recovery in the fresh manures; while the differences in recovery between the solid fresh and leached are slight, the differences between the solid and liquid, leached and fresh, are more considerable.

As to the dry matter produced, following are the figures:

1899.	1900.
Series 5.... 20.9 per cent.	Series 5.... 15.7 per cent.
Series 6.... 83.3 per cent.	Series 6.... 57.7 per cent.

It appears from these that in 1899, the increased yield over the check plot was greater in the case of the solid, and of the solid and liquid, leached. Also, here it is evident that the differences in yield from the solid and the solid and liquid, leached, are not as great as they were in 1899. Furthermore, the dry matter produced from the solid manure, leached, is proportionately richer in nitrogen than the dry matter produced from the solid and liquid manure, leached. This is true for both 1899 and 1900.

THE RELATIVE AVAILABILITY OF THE NITROGEN IN THE FORM OF NITRATE, AMMONIA, AND OF ORGANIC MATTER IN DRIED BLOOD.

The same amounts of nitrate nitrogen, of ammonia and of organic nitrogen, as dried blood, were applied on the several series, as in the years 1898 and 1899. Series 8, 10, 12, 14 and 16 received each the double quantity, that is, an amount of sodium nitrate containing 1.55 gram of nitrogen. Series 7 received 0.78 gram of nitrate nitrogen. On 17 and 18, enough ammonium sulphate and dried blood, respectively, were applied to furnish, approximately, the double nitrate quantity of 1.55 grams of nitrogen. The basis of comparison, therefore, will be Series 8. As in 1899, the proportionate recovery from Series 8 is slighter than that from Series 7. The differences, however, are somewhat smaller. The amounts recovered for 7 and 8 are 75.8 per cent. and 69.0 per cent., respectively, the corresponding figures for 1900 being 80.43 and 76.30 per cent. It would seem that the heavy showers in 1900 did not wash the nitrate beyond the reach of the crop. The dry matter in

1900, as was also the case in 1899, is richer in nitrogen on Series 8. In 1899 it was 1.268 per cent. for Series 7, and 1.330 per cent. for Series 8, and in 1900, 1.072 per cent. for Series 7, and 1.199 per cent. for Series 8. The absolute amount of nitrogen taken out is, naturally enough, greater on Series 8 than it is on Series 7. In 1899 it was 1.422 grams on 7, and 1.901 grams on 8—a greater proportionate increase on 7, and a greater absolute increase on 8.

The dry matter on Series 17, where ammonium sulphate was used, is richer in nitrogen than the dry matter on Series 18, where dried blood was used. The corresponding figures are 1.171 per cent. for 17, and 1.079 per cent. for 18, in 1900, as compared with 1.394 per cent. for 17 and 1.366 per cent. for 18, in 1899. It will be noticed that the differences are slighter in 1899. The percentage of nitrogen recovered is greater from the ammonia than it is for the dried blood, which is in agreement with the results of 1899. As with the nitrate, the percentage recovery from the ammonium sulphate and from the dried blood was greater in 1900. The recovery in 1899 was 50.3 for the ammonium sulphate, and 40.4 per cent. for the dried blood. The corresponding figures for 1900 are 68.84 per cent. and 52.15 per cent.; also due, no doubt, to a more generous supply of moisture. It thus follows that the availability of the ammonia and blood nitrogen was increased by the greater precipitation. It is interesting to note here that the recovery from the dried blood in 1900 was greater than that from the ammonium sulphate in 1899, both relatively and absolutely.

THE EFFECT OF THE USE OF THE SOLID AND OF THE SOLID AND LIQUID PORTIONS OF COW MANURE, FRESH AND LEACHED, WITH NITROGEN IN THE FORM OF NITRATE, OF AMMONIA AND OF ORGANIC MATTER.

The object of these combinations was not alone the study of the availability of the different forms of nitrogen when applied together, but also to determine whether the nitrogen of the nitrates applied as such, or formed from the materials applied, would be set free by the deoxidizing action of certain bacteria.[1] As in previous years, the clear manure, free from any admixture of litter was used, and the amount of manure applied was in no case much greater than that applied in actual practice.

[1] N. J. Sta. Rep., 1899, pp. 97-101; 1900, pp. 100-102.

By applying the different forms singly and also in combination, it becomes possible to determine, not only the comparative availability, but also the extent of denitrification, if any should take place. The results of 1898, and of 1899, have shown clearly that, thanks to the combination, the nitrogen in the different forms is even more efficient than where these forms are used singly. The reason for this we must seek in the fact that no single form is so well adapted to nourish the plant continually and uniformly as are the proper combinations. Such uniform feeding not only enables a uniform and healthy growth, but it also makes possible a more thorough utilization of the plant food made available by providing a better root system. It should also be remembered that the character of the season is an important factor in determining the relative availability of the different forms of nitrogen. A more abundant supply of moisture will tend to increase the availability of the organic forms and will also tend to increase to a still greater extent, proportionately, the availability of the nitrogen in the different combinations. However, while the tendency is there, the combinations do not always show a proportionate increase over the forms used singly. The following table shows the actual average percentage recovery of nitrogen, when the materials furnishing it were used singly, as well as when they were used in combination, together with the percentage increase of nitrogen from combinations of two materials, calculated from the increase obtained when they were used singly.

The difference between the percentage of nitrogen actually recovered and the percentage recoverable, calculated, represents the losses due to all causes; the difference is expressed in percentage in the last column. It appears that in 1900, the percentage recovery was greater in nine out of eighteen series, and of these nine, six were in series where the materials applied were used singly. This is particularly true of 6, 7, 8, 17 and 18. On the other hand, the percentage recovery is greater in 1899, in the series where the combinations of the different forms were used, that being especially noticeable in Series 10, 11, 12, 13 and 14. While it may be assumed that the greater availability of the nitrate, ammonia and dried blood was due in 1900 to a greater abundance of moisture, it is more difficult to determine the causes that were responsible for a slighter percentage of recovery on the series where

TABLE III.

	Series.	1899. Nitrogen recovered.	1899. Calculated recovery.	1899. Nitrogen not recovered in the combinations of materials.	1900. Nitrogen recovered.	1900. Calculated recovery.	1900. Nitrogen not recovered in the combinations of material.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Solid manure, fresh	3	8.3			10.81		...
Solid and liquid, fresh	4	40.2			30.60		...
Solid, leached	5	8.4			7.38		...
Solid and liquid, leached	6	13.8			22.06		...
Sodium nitrate	7	75.8			80.43		...
Sodium nitrate	8	69.0			76.30		...
Ammonium sulphate	17	50.3			68.84		...
Dried blood	18	40.4			52.15		...
7 and 3 in	9	16.4	21.12	22.2	19.97	22.10	9.64
8 and 3 in	10	29.4	27.59		27.99	28.95	3.32
7 and 4 in	11	46.5	44.74		41.43	38.76	...
8 and 4 in	12	46.8	46.71		44.68	43.42	...
7 and 5 in	13	21.3	27.59	23.0	17.50	19.33	9.47
8 and 5 in	14	35.1	35.15		24.25	26.68	9.11
7 and 6 in	15	21.6	22.92	5.8	31.71	31.41	...
8 and 6 in	16	29.1	27.89		38.32	37.10	...
17 and 5 in	19	27.9	27.35		20.63	24.24	14.89
18 and 5 in	20	23.3	22.51		19.20	19.56	1.84

combinations were used. It is questionable in just how far the difference may be attributed to leaching in 1900, for the fact that the recovery from the double quantity of nitrate on Series 8 was greater in that year than was the case in 1899, would indicate that but little, if any, of the nitrate nitrogen was washed beyond the reach of the plant roots. The differences in the amount of nitrogen applied may have had something to do with it; even that is questionable, for the percentage recovery was slighter in 1900 on Series 11 and 12, where more nitrogen was applied in 1899, as well as on Series 13 and 14, where more nitrogen was applied in 1900. It is possible that the differences were due to denitrification, still for the present this is only surmise.

As it is, the percentage of nitrogen recovered in 1900 exceeds the calculated recovery in four cases out of ten. They are Series 11, with a recovery of 41.43 per cent., calculated 38.76 per cent.;

Series 12, with a recovery of 44.68 per cent., calculated 43.42 per cent.; Series 15, with a recovery of 38.32 per cent., calculated 37.10 per cent. In Series 15 and 16, where leached manure was used with nitrate, the percentage of nitrogen recovered differs to a greater extent from that of 1899. The figures for 1889 were 21.6 per cent. and 29.1 per cent., as against 31.71 per cent. and 38.23 per cent. in 1900. The losses varied from 1.84 per cent. on Series 20, to 14.89 per cent. on Series 19. In 1899 the maximum loss was 23 per cent. on Series 13—the minimum loss, 5.8 per cent. on Series 15.

That the season has much to do with the production and transformation of plant food in the soil is brought out very graphically in the following columns, where the availabilities of the several nitrogenous substances are compared.

TABLE IV.

	Corn. 1898.	Oats. 1899.	Oats and millet. 1899.	Oats. 1900.	Oats and corn. 1900.
Sodium nitrate.....	100.0	100.0	100.0	100 0	100.0
Ammonium sulphate.....	99.5	72.9	77.9	90.22	87.75
Dried blood.....	95.4	58.5.	61.3	68.35	73.07
Solid manure, fresh	16.76	12.0	43.1	14.16	26.36
Solid manure, leached.....	37.87	12.1	46.4	9.67	21.99
Solid and liquid, fresh.....	49.66	58.2	88.4	40.10	51.46
Solid and liquid, leached ..	50.38	20.0	33.0	28.91	35.91

As was already pointed out in the report of 1900,[1] the superiority of the solid and liquid manure over the solid manure is brought out strikingly. Moreover, it appears from the later results that the solid manure, fresh, if anything, is superior to the solid manure, leached, which is contrary to what could be drawn from the results obtained in 1898. In 1899, the solid fresh, and the solid leached, showed the same rate of availability. In 1900, the solid fresh, in the oat crop alone, and in the oats and corn taken together, showed a higher rate of availability. Similarly, in the case of the solid and liquid, fresh and leached, the availability was practically the same in 1898. It was higher for the fresh in 1899, and also in 1900.

RESULTS OF THE CORN EXPERIMENT—RESIDUAL EFFECTS.

The oats were harvested on July 6th. A few days later the soil in each cylinder was dug up, and thoroughly stirred. One

[1] N. J. Sta. Rep., 1900, p. 102.

hundred kernels of corn were planted in each cylinder with the twofold object of exhausting the nitrogen left over from the crop just harvested, and also of determining the influence of the residual nitrogen on plant growth. In using a considerable quantity of seed, it was intended to make the exhaustion more rapid and complete, and at the same time, to insure greater uniformity of assimilation by eliminating, to a great extent, the influence of defective individual plants. By this means the average is made more truly representative.

TABLE V.—RESULTS OF THE CORN EXPERIMENT.

Series.		Residual nitrogen.	Dry matter in crop.	Nitrogen in dry matter.	Nitrogen in crop.	Increase over check plot.	Per cent. of nitrogen recovered.	Average per cent. of residual nitrogen recovered.	Both crops. Increase over check plot.	Both crops. Per cent. of nitrogen recovered.	Average.
		Grams.	Grams.	Per ct.	Grams.	Grams.			Grams.		
1	A		145.0	0.617	0.895						
	B		117.3	0.691	0.810						
	C		125.2	0.694	0.868						
2	A		135.1	0.579	0.782						
	B		124.4	0.649	0.807	(0.794)		...			
	C		124.0	0.640	0.794		...				
3	A	3.57	193.6	0.624	1.207	0.413	11.57		0.895	22.10	
	B	3.48	175.9	0.605	1.064	0.270	7.76	10.02	0.839	20.72	19.78
	C	3.79	201.7	0.596	1.201	0.407	10.74		0.669	16.52	
4	A	2.48	201.0	0.581	1.168	0.374	15.08		1.878	47.19	
	B	2.90	178.9	0.645	1.153	0.359	12.38	11.75	1.434	36.03	38.61
	C	2.90	159.4	0.640	1.020	0.226	7.79		1.301	32.61	
	A	3.67	224.4	0.577	1.294	0.500	13.62		0.819	20.53	
	B	3.78	178.9	0.589	1.055	0.261	6.90	9.86	0.473	11.85	16.50
	C	3.64	169.8	0.662	1.124	0.330	9.07		0.683	17.12	
6	A	3.07	162.2	0.603	0 977	0.183	5.96		1.151	28.49	
	B	3.12	155.9	0.627	0.978	0.184	5.90	6.25	1.099	27.20	26.94
	C	3.25	139.8	0.729	1.018	0.224	6.89		1.015	25.12	
7	A	0.11	126.7	0.660	0.836	0.042	38.18		0.728	93.33	
	B	0.21	103.9	0.660	0.685	0.109			0.459	58.85	72.22
	C	0.15	98.0	0.685	0.671	0.123			0.503	64.49	
8	A	0.32	125.1	0.618	0.773	0.021			1.210	78.06	
	B	0.40	133.0	0.630	0.838	0.044	11.00		1.196	77.16	75.03
	C	0.38	105.7	0.674	0.712	0.082			1.083	69.87	

Series.		Residual nitrogen.	Dry matter in crop.	Nitrogen in dry matter.	Nitrogen in crop.	Increase over check plot.	Per cent. of nitrogen recovered.	Average per cent. of residual nitrogen recovered.	Both crops. Increase over check plot.	Both crops. Per cent. of nitrogen recovered.	Average.
		Grams.	Grams.	Per. ct.	Grams.	Grams.			Grams.		
9	A	3.85	215.4	0.618	1.330	0.536	13.92		1.516	31.39	27.89
	B	3.86	189.6	0.601	1.139	0.345	8.95	9.91	1.314	27.20	
	C	3.89	158.5	0.670	1.061	0.267	6.86		1.211	25.07	
10	A	4.16	202.2	0.575	1.162	0.368	8.85		1.806	32.25	35.66
	B	3.76	237.6	0.573	1.361	0.567	15.08	10.80	2.405	42.95	
	C	4.17	189.8	0.605	1.147	0.353	8.47		1.779	31.77	
11	A	2.52	187.8	0.633	1.188	0.394	15.63		2.631	55.27	48.14
	B	3.11	185.1	0.627	1.160	0.366	11.77	11.56	2.015	42.33	
	C	2.73	166.0	0.598	0.993	0.199	7.29		2.229	46.83	
12	A	2.73	225.0	0.591	1.330	0.536	19.36		3.333	60.27	51.62
	B	3.20	183.6	0.645	1.184	0.390	12.19	12.92	2.716	49.11	
	C	3.24	170.4	0.598	1.019	0.225	6.94		2.515	45.48	
13	A	3.92	255.3	0.527	1.344	0.550	14.03		1.402	29.39	26.90
	B	3.98	182.4	0.578	1.052	0.258	6.48	11.42	1.047	21.95	
	C	3.91	226.3	0.589	1.332	0.538	13.76		1.401	29.37	
14	A	4.12	224.8	0.556	1.250	0.456	11.07		1.871	33.77	31.07
	B	4.21	195.6	0.608	1.190	0.396	9.41	9.03	1.727	31.17	
	C	4.25	174.3	0.617	1.075	0.281	6.61		1.566	28.27	
5	A	3.07	200.0	0.588	1.177	0.383	12.47		2.135	44.29	38.95
	B	3.35	185.9	0.606	1.127	0.333	9.94	10.66	1.805	37.45	
	C	3.46	172.8	0.652	1.125	0.331	9.57		1.692	35.10	
16	A	3.09	206.6	0.555	1.146	0.352	11.39		2.850	50.98	43.80
	B	3.47	189.7	0.580	1.099	0.305	8.79	8.95	2.425	43.38	
	C	3.77	160.5	0.641	1.046	0.252	6.68		2.070	37.03	
17	A	0.45	115.9	0.649	0.752	0.042			1.027	67.57	65.84
	B	0.49	131.8	0.621	0.819	0.025	5.10		1.050	69.08	
	C	0.47	92.7	0.728	0.674	0.120			0.925	60.86	
18	A	0.74	137.2	0.646	0.886	0.092	12.43		0.839	56.31	54.83
	B	0.66	120.6	0.670	0.808	0.014	2.12	5.48	0.847	56.85	
	C	0.74	120.5	0.671	0.808	0.014	1.89		0.765	51.34	
19	A	4.58	173.7	0.652	1.132	0.338	7.38		1.272	23.09	27.02
	B	4.22	174.1	0.654	1.139	0.345	8.18	8.08	1.637	29.71	
	C	4.33	174.6	0.670	1.170	0.376	8.68		1.557	28.26	
20	A	4.44	182.9	0.667	1.220	0.426	9.60		1.461	26.66	26.48
	B	4.48	174.9	0.677	1.184	0.390	8.71	9.02	1.388	25.33	
	C	4.36	170.7	0.689	1.175	0.381	8.74		1.504	27.45	

TABLE VI.—AMOUNT OF RESIDUAL NITROGEN AND PROPORTION RECOVERED.

	Millet, 1899.			Corn, 1900.		
Series	Taken out by the oats.	Residual nitrogen. Grams.	Average per cent. of residual nitrogen recovered. Per cent.	Taken out by the oats.	Residual nitrogen. Grams.	Average per cent. of residual nitrogen recovered. Per cent.
1	...	...	...		...	
2	...	...	...		...	
3	8.3	3.04	17.5	10.81	3.61	10.02
4	40.2	3.14	15.9	30.60	2.76	11.75
5	8.4	1.80	19.2	7.38	3.70	9.86
6	13.8	3.90	5.5	22.06	3.15	6.25
7	75.8	0.19	...	80.42	0.16	
8	69.0	0.48	...	76.30	0.37	
9	16.4	3.43	12.7	19.97	3.87	9.91
10	29.4	3.44	17.8	27.99	4.03	10.80
11	46.5	3.23	16.8	41.43	2.79	11.56
12	46.8	3.61	21.8	44.68	3.06	12.92
13	21.3	2.16	6.8	17.50	3.94	11.42
14	35.1	2.28	10.6	24.25	4.19	9.03
15	21.6	4.16	5.9	31.71	3.29	10.66
16	29.1	4.31	6.9	38.32	3.44	8.95
17	50.3	0.81	...	68.84	0.47	
18	40.4	0.92	...	52.15	0.71	5.48
19	27.9	2.58	7.5	20.63	4.38	8.08
20	23.3	2.69	11.1	19.20	4.43	9.02
Average		2.56	12.6		2.91	9.17

The figures again bring out the facts already noted in 1899. In all cases where manure had been applied, the plants were enabled to secure a larger amount of nitrogen than those on the check plot. More than that, the series where solid manure alone was applied, yielded more nitrogen in the residual crops, as compared with the series on which solid and liquid manure was applied. On the other hand, there was no gain over the check plot from the sodium nitrate and ammonium sulphate; in fact, there was even a slight loss. In the case of the dried blood, there was a small gain over the check plot. Hence it may be said here that there was no *residual* effect from the nitrate and the ammonia, and a very slight effect from the dried blood. Owing to a more uniform germination of the seed, the corn produced results also more uniform as compared with the millet of 1899. It will be observed that the yield of nitrogen on Series 2 was even slighter

than that on Series 1, differing in this respect from the millet. Also this crop shows a percentage of nitrogen higher than the average in the dry matter on all of the series where there was not residual effect, as well as on the first two series, where no nitrogen was applied. Of the residual nitrogen, proportionately less was recovered in 1900. There was, on the average, 2.56 grams of residual nitrogen in each series in 1899, and 2.91 grams in 1900. Of that, there was recovered 12.6 per cent. in 1899, and 9.71 per cent. in 1900. The last figures represent the average per cent. recovery from fourteen series in 1899 and from fifteen in 1900.

THE AVAILABILITY OF THE RESIDUAL NITROGEN IN THE SOLID AND IN THE SOLID AND LIQUID PORTIONS OF FRESH MANURE, AND ALSO OF LEACHED MANURES.

In 1899 there were 3.04 grams of residual nitrogen on Series 3, and 3.14 grams on Series 4, when the oats were harvested. In 1900, there were 3.61 grams of residual nitrogen on Series 3, and 2.76 grams on Series 4. Of that nitrogen, there was recovered by the millet 17.8 per cent. on Series 3, and 15.9 per cent. on Series 4, while the corn recovered 10.02 per cent. on Series 3 and 11.75 per cent. on Series 4. It appears that the recovery in 1899 was greater than that in 1900, and furthermore the solid manure does not make as good a showing in 1900, as compared with the solid and liquid manure. This is applicable to both the fresh and leached manure. Thus the recovery from the solid and liquid manure, fresh, was greater, relatively than the recovery from the solid manure, which is contrary to the experience of 1899. However, Tables VII and VIII show that the absolute amounts of nitrogen furnished by the solid manure to the residual crops are greater than those supplied by the solid and liquid portions. The same is true of the leached manures. The solid portion yielded in 1899, 1.398 grams of nitrogen, and the solid and liquid portions yielded in 1899, 1.269 grams. The corresponding figures for 1900 are 1.158 grams for the solid, leached, and 0.991 gram for the solid and liquid, leached. In 5 and 6 the residual nitrogen was, in 1899, 1.80 grams and 3.90 grams, respectively, and of that there was recovered 19.2 per cent. for 5, and 5.5 per cent. for 6. In 1900 the residual nitrogen amounted to 3.70 grams in 5, and 3.15 per cent. in 6, and of that there was yielded in the corn 9.86 per cent. for 5, and 6.25 per cent.

TABLE VII.—NITROGEN IN THE CORN OF 1900—THE STUDY OF RESIDUAL EFFECTS.

Series.	Average weight of nitrogen in crop. Grams.	Average per cent. of nitrogen in crop. Per cent.
1	0.858	0.667
2	0.794	0.629
3	1.157	0.608
4	1.114	0.622
5	1.158	0.609
6	0.991	0.653
7	0.731	0.668
8	0.774	0.641
9	1.177	0.629
10	1.223	0.584
11	1.114	0.619
12	1.178	0.611
13	1.243	0.565
14	1.172	0.594
15	1.143	0.615
16	1.097	0.592
17	0.748	0.666
18	0.834	0.662
19	1.147	0.659
20	1.193	0.678

TABLE VIII.—NITROGEN IN THE MILLET OF 1899—THE STUDY OF RESIDUAL EFFECTS.

1	1.000	2.514
2	1.052	1.223
3	1.582	1.176
4	1.558	1.160
5	1.398	1.239
6	1.269	1.322
7	0.878	1.304
8	0.854	1.425
9	1.487	1.441
10	1.661	1.234
11	1.598	1.291
12	1.834	1.132
13	1.199	1.143
14	1.292	1.115
15	1.296	1.256
16	1.347	1.409
17	0.948	1.301
18	0.961	1.305
19	1.245	1.283
20	1.352	1.493

for 6. As in the previous year, the varying amounts of residual nitrogen rendered the problem more complicated; for all that, it appears that the greater the proportionate amount of soluble nitrogen in the manure applied, the smaller the amount of nitrogen recovered in the residual crop. Of the manure applied in 1899, there was contained in the solid portion 0.220 per cent. of soluble nitrogen. The residual crop obtained from Series 3, on the average, 1.582 grams of nitrogen and from Series 4, on the average, 1.558 grams of nitrogen, notwithstanding the fact that there was applied on Series 4, 5.25 grams of nitrogen as against 3.32 grams on Series 3. Similarly in 1900, the solid portion, fresh, contained 0.066 per cent. of soluble nitrogen, and the solid and liquid portion, fresh, 0.269 per cent. of soluble nitrogen. The residual crop obtained from Series 3, 1.157 grams of nitrogen and from Series 4, 1.114 grams of nitrogen; the same relations hold true, even more markedly, in the leached manures. The reason for the above is quite apparent if we consider that it is the soluble nitrogen in the manure that is rapidly changed, and having once undergone the change it is like nitrate in that it is largely lost to the crop if not taken up within a short time. The figures clearly indicate that there is no residual effect from the nitrate, and hence the more rapidly a given manure is nitrified, the smaller, everything else being equal, will be its residual effect. It should also be noted here, that in the case of the solid, leached, the residual crop appropriated more nitrogen than the first crop. This is true of both the millet and the corn. Subtracting the amount of nitrogen obtained from the check plots we find that the oats in 1900 obtained from the solid manure, leached, 0.295 gram of nitrogen, while the corn following the oats obtained from the residue 0.364 gram of nitrogen. Similarly, the oats in 1899 obtained from Series 5, 0.165 gram of nitrogen, while the millet following the oats obtained 0.346 gram of nitrogen.

THE AVAILABILITY OF THE RESIDUAL NITROGEN IN THE FORM OF NITRATE, AMMONIA, AND OF ORGANIC MATTER IN DRIED BLOOD.

It was already noted that from the nitrate, both 5 and 10 grams, and from the ammonia, no residual effect was obtained. The yield of nitrogen on Series 2 was 0.799 gram. On Series 7, where 5 grams of nitrogen were applied, the yield was 0.731 gram, and on

Series 8, with the double quantity of nitrate, the yield of nitrogen in the crop was 0.774 gram, so there was actually less nitrogen gathered by the residual crop from 7 and 8 than there was from the blank series. A similar observation was made in 1899, and the explanation seems to be that with the aid of the minerals and the nitrate, stronger plants are developed on 7 and 8 than there are on 2, and these, because of their better developed root system, are enabled to get more nitrogen out of the soil itself and thus leave it poorer. This view is supported by a comparison of the yields on Series 1 and 2. It will be noticed that the residual corn crop obtained more nitrogen from Series 1 than it did from Series 2. Now, no nitrogen has been added to either for three years, but minerals were applied on Series 2, and these enabled the crops to withdraw more nitrogen from the soil as a study of the analytical data will show. In like manner, on Series 17 there was no residual effect, and the nitrogen gathered by the corn was only 0.748 gram less than that obtained from Series 2. Above all things it seems clear that no residual effect need be expected from ammonium sulphate. It should be remembered that the residual crops were planted within a few days after the oat crops were harvested. On Series 18 there was a slight gain over Series 2, indicating that there was at least a small residue of nitrogen left for the corn. In 1899 no such effect was observed on 18, and should further experience prove that there is some residual effect from dried blood it can by no means be very great. Hence, as in 1899, we are confronted by the fact that although but 52.15 per cent. of nitrogen was recovered from the amount applied as dried blood, but 68.84 per cent. from that applied as ammonium sulphate, and but 76.30 per cent. from that applied as nitrate, no further benefit to succeeding crops need be expected from those particular applications. If anything, the availability of these three forms of nitrogen was slightly exaggerated because of the greater amounts of nitrogen taken out of the soil with their cooperation, nitrogen that was credited to them.

THE EFFECT OF THE USE OF THE SOLID AND OF THE SOLID AND LIQUID PORTIONS OF COW MANURE, FRESH AND LEACHED, ALONE, AND WITH NITROGEN IN THE FORM OF NITRATE, OF AMMONIA AND OF ORGANIC MATTER.

In the table submitted below are given the amounts of nitrogen

applied, the percentage of the applied nitrogen recovered in the residual crop, the residual nitrogen after that crop, and the percentage of nitrogen obtained from the residue by the residual crop.

TABLE IX.

Series.	Total nitrogen applied. Grams.	Nitrogen recovered. Per cent.	Residual nitrogen. Grams.	Nitrogen recovered. Per cent.
3	4.05	8.96	3.61	10.02
4	3.98	8.04	2.76	11.75
5	3.99	9.12	3.70	9.86
6	4.04	4.88	3.15	6.25
7	0.78	...	0.16	...
8	1.55	...	0.37	...
17	1.52	...	0.47	...
18	1.49	2.68	0.71	5.48
9	4.83	7.93	3.87	9.91
10	5.60	7.66	4.03	10.80
11	4.76	6.72	2.79	11.56
12	5.53	6.94	3.06	12.92
13	4.77	9.41	3.94	11.42
14	5.54	6.80	4.19	9.03
15	4.82	7.24	3.29	10.66
16	5.59	5.42	3.44	8.95
19	5.51	6.41	4.38	8.08
20	5.48	7.28	4.43	9.02

The relations pointed out in the last report largely hold true also this year. The recovery in the combinations does not differ much from the recovery in the manures alone, which might be expected, since the dried blood shows but a very slight residual effect. It should again be emphasized here that the tabulated figures show less favorably for the manures used in combination than is actually the case, for as a matter of fact the recovery from the nitrate plots was less than from Series 2, which was used as the standard of comparison. In 1899 the solid, leached, showed the greatest variation in recovery, the figures being 19.2 per cent. for 5, and only 6.8 per cent. and 10.6 per cent., respectively, for 13 and 14. In 1900 the results are more uniform. The recovery for 5 is 9.86 per cent. of the residual nitrogen (Table IX), while the average recovery from 13, 14, 19 and 20, where 5 was used in combination with 7, 8, 17 and 18, is 9.37 per cent. Similarly the recovery from 3 is 10.02 per cent., and the average recovery from 9 and 10 is 10.35 per cent. The recovery from 4 is 11.75 per cent., and the average recovery from 11 and 12 is 12.24 per cent. In

Series 6 the recovery was 6.25 per cent., while the average recovery in 15 and 16 was 9.80 per cent., showing a considerable increase for the two, an increase that was not quite as marked in 1899. The maximum residual recovery was 12.92 per cent. in Series 12; the minimum residual recovery was 5.48 per cent. in Series 18. In 1899, the maximum residual recovery was 21.8 per cent. in 12, and the minimum residual recovery 5.5 per cent. in 6.

THE AVAILABILITY OF THE NITROGEN IN THE DIFFERENT MATERIALS USED WHEN THE COMBINED RESULTS OF THE TWO CROPS, OATS AND CORN, ARE CONSIDERED.

Because of a more favorable season, the availability of the nitrate, ammonia, and of the dried blood, was higher than it was in 1899. Not alone was there a greater quantity of nitrogen taken out of the check plots, but it also seems that on the nitrate, ammonia and dried blood plots, there was a proportionately larger quantity taken out of the soil. This assumption is justified by the results obtained from the residual crops on the series named. It follows from this that when the first crop is taken alone, the availability of the three forms mentioned is placed somewhat above its true value. On the other hand, the exhaustion of the humus on these series would modify the soil to such an extent as to influence the yields appreciably. It is for these reasons that the returns from the combinations cannot be expected to be almost exactly equal to the sum for the series where the materials are used singly. Aside from the slight discrepancies, however, the agreements are more than satisfactory.

From quick-acting materials immediate returns are expected, and no residual effects are looked for. Hence, they are at a disadvantage when compared with slowly decaying organic materials through two or more crops. This was already pointed out in last year's report. It was also noted then that on account of the smaller returns in the residual crop from 7, 8, and 17 as compared with Series 2, the percentage recovery of these materials is somewhat lowered, since the losses shown for these materials in the residual crop must be subtracted from the gains made in the oat crops. A more detailed discussion of this point in question was presented elsewhere.[1] The following table shows the percentage recovery of nitrogen for all of the series when the two crops are

[1] N. J. Sta. Rep., 1900, p. 108.

used as the basis of calculating, as well as the calculated recovery of those series where the combinations of materials was used.

TABLE X.

	Series.	Nitrogen recovered. Per cent.	Calculated recovery. Per cent.	Nitrogen not recovered in the combinations of materials. Per cent.
Solid manure, fresh.....	3	19.78		
Solid and liquid, fresh ...	4	38.61		
Solid, leached	5	16.50		
Solid and liquid, leached.	6	26.94		
Sodium nitrate.....	7	72.22		
Sodium nitrate.....	8	75.03		
Ammonium sulphate.....	17	65.84		
Dried blood	18	54.83		
7 and 3 in	9	27.89	28.94	1.24
8 and 3 in	10	35.66	35.07	
7 and 4 in	11	48.14	44.14	
8 and 4 in	12	51.62	48.84	
7 and 5 in	13	26.90	25.60	
8 and 5 in	14	31.07	32.87	5.48
7 and 6 in	15	38.95	34.25	
8 and 6 in	16	43.80	40.27	
17 and 5 in	19	27.02	30.11	10.26
18 and 5 in	20	26.48	26.92	1.63

The figures show that in six cases out of ten there was a gain on the combinations over the sum of the increase on the materials when they were used singly. Of the other four, 9 and 20 show but slight differences, and may be disregarded, and on 14 and 19 the losses were 5.48 and 10.25 per cent., respectively. It is evident from the results, that there was no denitrification, and this confirms the experience of last year.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 66.]

ON THE COMPOSITION OF THE FERROCYANIDES OF ZINC.

BY EDMUND H. MILLER AND J. L. DANZIGER.

Received June 7, 1900.

THIS work was undertaken to determine the ratios of iron, potassium and zinc in the potassium zinc ferrocyanides, when precipitated under certain definite conditions in view of the contradictory statements which have appeared regarding their composition. The precipitates were all formed in large beakers in the

cold, using zinc sulphate and potassium ferrocyanide. When zinc was to be in excess 100 grams of zinc sulphate and 50 grams of potassium ferrocyanide were used, while for ferrocyanide in excess 100 grams potassium ferrocyanide to 50 grams of zinc sulphate were taken. They were lettered to correspond with those of cadmium described in this Journal, **24**, 226.

DESCRIPTION OF PRECIPITATES.

A. Neutral solution, zinc in excess; white gelatinous precipitate which became granular on washing.

B. Neutral solution, ferrocyanide in excess; white curdy precipitate settled by adding magnesium chloride.

C. Hydrochloric acid solution containing 10 cc. (sp. gr. 1.2 per liter) zinc in excess; bluish white curdy precipitate.

D. Hydrochloric acid solution, same with ferrocyanide in excess; pure white curdy precipitate.

E. Acetic acid solution containing 10 cc. (50 per cent. acetic acid per liter) zinc in excess; pure white flocculent precipitate, changing to a granular form after a few washings.

F. Acetic acid solution, same with ferrocyanide in excess; white precipitate which settles badly.

G. Ammoniacal solution, zinc in excess; formed by adding ferrocyanide to a solution of zinc hydroxide in ammonia, pure white and settled well.

H. Ammoniacal solution, ferrocyanide in excess; made in same way but settled very badly.

I. Zinc acetate and potassium ferrocyanide; no free acid was added but as the zinc acetate contained a trace of acetic acid the conditions were between *A* and *E*.

In general the precipitates were very difficult to wash when ferrocyanide was in excess, but the addition of magnesium chloride helped them to settle so that the most troublesome was clean when washed twenty-five times. They are all soluble in concentrated hydrochloric acid.

The method of analysis was in all cases the same, the object being to get the ratio between zinc and iron, but in some cases, especially when magnesium chloride was used to make the precipitates settle, the potassium was also determined to confirm the iron-zinc ratio.

Portions of the moist precipitate, judged to contain about 1 gram, were put in casseroles and about 50 cc. of hydrochloric acid (sp. gr. 1.2) added; then heated till completely dissolved. Twenty-five cc. of nitric acid were next added and the whole evaporated nearly to dryness, taken up with hydrochloric acid, and evaporated to 10 cc. After dilution the iron was separated from the zinc by one basic acetate precipitation and two precipitations with ammonia and ammonium chloride, ignited and weighed as ferric oxide. In the filtrate the zinc was precipitated as sulphide, dissolved in hydrochloric acid, precipitated as $ZnNH_4PO_4$ by $(NH_4)_2HPO_4$ and weighed as $Zn_2P_2O_7$. When potassium was also to be determined the iron and zinc were taken out as sulphide to avoid the accumulation of ammonium salts, and the potassium finally weighed as sulphate.

RESULTS OF ANALYSES OF PRECIPITATES.

All the analyses were made in duplicate and when a satisfactory agreement was not obtained the work was repeated. In order to save space only the final results are given in the following table:

Precipitate.	Remarks.	Ratio found, Fe : K : Zn.	Corresponding formula.	Theoretical ratio, Fe : K : Zn.
A.	Two weeks after precipitation ..	1 : ... : 1.51	$K_2Zn_3(Fe(CN)_6)_2$	1 : 1 : 1.50
A.	After standing ..	1 : 0.81 : 1.59	$K_4Zn_5(Fe(CN)_6)_5$	1 : 0.8 : 1.60
B.	Fresh precipitate	1 : ... : 1.35	$K_4Zn_4(Fe(CN)_6)_3$	1 : 1.33 : 1.33
B.	After standing ..	1 : ... : 1.49	$K_2Zn_3(Fe(CN)_6)_2$	1 : 1 : 1.50
B.	After five days' heating	1 : 1.02 : 1.51	$K_2Zn_3(Fe(CN)_6)_2$	1 : 1 : 1.50
C.		1 : ... : 1.50	$K_2Zn_3(Fe(CN)_6)_2$	1 : 1 : 1.50
D.		1 : ... : 1.40	$K_6Zn_7(Fe(CN)_6)_5$	1 : 1.2 : 1.40
E.		1 : ... : 1.51	$K_2Zn_3(Fe(CN)_6)_2$	1 : 1 : 1.50
F.		1 : ... : 1.43	$K_6Zn_7(Fe(CN)_6)_5$	1 : 1.2 : 1.40
G.	Washed with water	1 : 0 : 2.46		
G.	Washed with ammonia	1 : 0 : 2.00	$Zn_2Fe(CN)_6$	1 : 0 : 2.00
H.		1 : 0 : 1.97	$Zn_2Fe(CN)_6$	1 : 0 : 2.00
I.		1 : ... : 1.51	$K_2Zn_3Fe(CN)_6$	1 : 1 : 1.50

We see from this table, (1) that from *A* and *B*, the composition changes on standing; (2) that the composition of the precipitates is entirely different from what Stone[1] and Van Ingen found under similar but not identical conditions; (3) that in hydrochloric acid

[1] This Journal, 19, 544 (1897).

solution, with zinc in excess (*C*), the results agree with Wyrouboff,[1] De Koninck and Prost,[2] and Miller and Mathews;[3] with ferrocyanide in excess (*D*), the results agree with those of Miller and Mathews;[3] (4) that in an acetic acid solution, the composition is but slightly different from that formed in a hydrochloric acid solution; this explains why Galetti's[4] titration results do not agree with his theory; (5) that in an ammoniacal solution, the normal ferrocyanide is precipitated, whichever is in excess as given by Moldenauer,[5] but when zinc is in excess zinc hydroxide is carried down.

In order to show whether these ferrocyanides are mixtures of simple ferrocyanides or whether they are definite compounds, a method of separation must be employed. Two methods are available, one mechanical and the other chemical. It was noticed that in washing the precipitates one portion would always settle well, while another portion would invariably remain in suspension.

In the work on cadmium, it was shown in one case, that the composition of the precipitate that remained in suspension was $CdK_2Fe(CN)_6$. This fact was made the basis of an attempt at a mechanical separation. A large amount of precipitate was made, in a large bottle, using zinc acetate (*I*). It was washed without loss, by causing the entire precipitate to settle by the use of strontium nitrate. It was then analyzed and gave the ratio of zinc to iron of 1.51 : 1.00, corresponding to $Zn_3K_2(Fe(CN)_6)_2$.

After the strontium nitrate had been entirely washed out, the precipitate did not settle well, and the supernatant liquid had a milky appearance, due to suspended ferrocyanide. This supernatant liquid was siphoned into a second large bottle and allowed to stand over night. Fresh water was poured on the original precipitate, thoroughly stirred and allowed to stand. The supernatant liquid in the second bottle, which was still of a milky appearance, was siphoned into a third bottle, in which strontium nitrate was present. This caused the precipitate to settle completely, leaving a clear solution above, which was siphoned off and rejected.

The residue in the second bottle was washed by the supernatant liquid from the first bottle, and the process continued until a suffi-

[1] *Ann. chim. phys.*, [5], II, 485 (1876).
[2] *Chem. News*, 76, 6 (1897).
[3] This Journal, 19, 547 (1897).
[4] *Bull. Soc. Chim.*, II, p. 83 (1864).
[5] *Chem. Ztg.*, No. 14 (1891).

cient amount of precipitate had collected in the third bottle to be analyzed. The residue in the last bottle gave the ratio of zinc to iron 1.50:1.00, corresponding again to $Zn_3K_2(Fe(CN)_6)_2$. The residue in the first bottle gave the same ratio, showing that no separation was effected.

During the work on cadmium ferrocyanides, it was found that when a complex precipitate was treated several times with strong ammonia, and the residue analyzed, it gave a formula corresponding to the normal ferrocyanide, $Cd_2Fe(CN)_6$. This same treatment was applied to the zinc ferrocyanides.

First precipitate (*E*) was treated with strong ammonia seven times and the residue analyzed. It gave the ratio of zinc to iron of 2:1, corresponding to $Zn_2Fe(CN)_6$. Then precipitate *I* was treated in the same manner and both the residue and ammoniacal solution were analyzed.

The ammoniacal solution was of a strong yellow color and, on dilution with water, a white precipitate separated, and as the ammonia evaporated, more precipitate formed. The analysis of the residue gave the ratio of zinc to iron of 1.97:1.00, corresponding to $Zn_2Fe(CN)_6$. The analysis of the precipitate from the ammoniacal solution gave the ratio of zinc to iron of 1.97:1.00, the same as the residue. The latter was not what was expected, for, if the precipitates are mixtures of different proportions of $Zn_2Fe(CN)_6$ and $ZnK_2Fe(CN)_6$, and the residues gave $Zn_2Fe(CN)_6$, the ammoniacal solution should have given $ZnK_2Fe(CN)_6$.

The fact that the residue from treating either *E* or *I* with ammonia is $Zn_2Fe(CN)_6$ agrees with the results on cadmium, but we have not so far succeeded in obtaining $K_2ZnFe(CN)_6$ either as a precipitate or from the ammoniacal solution.

After finishing this article it seemed so important to obtain, if possible, the compound $K_2ZnFe(CN)_6$ that two more precipitations were made in neutral solutions, one with a very small excess of zinc, the other with a very small excess of ferrocyanide, thus duplicating as closely as possible the conditions under which Stone and Van Ingen state the compound to be formed,—as we thought we might have had too great an excess in our previous experiments. The precipitates were washed and analyzed as usual. The ratios were Fe:Zn::1.00:1.58 when zinc was in ex-

cess and 1.00:1.46 when the ferrocyanide was in excess. These results are in accord with those given on page 825 and are at variance with those of Stone and Van Ingen.

As the solution obtained by treating the zinc ferrocyanides with ammonia undergoes decomposition with the formation of blue precipitates and soluble ferricyanides, it is intended to continue the investigation of the action of ammonia on the potassium cadmium ferrocyanides instead of on the zinc salts.

QUANTITATIVE LABORATORY,
June 4, 1902.

ON STANDARD TARTAR EMETIC AND ITS STRUCTURAL FORMULA.

BY F. E. HALE.

Received May 23, 1902.

GRUENER[1] has already shown that tartar emetic solutions containing about 16 grams of tartar emetic, 20-30 grams of tartaric acid, and 1-10 cc. of concentrated hydrochloric acid to the liter, will keep from five to twelve months without any change in strength. There is no deposit of antimonious oxide under these conditions, no oxidation, and no signs of fungous growth. Gruener determined the strength of his tartar emetic solutions by titration with a decinormal iodine solution, standardized by decinormal arsenite. The mean of twenty-nine determinations showed 43.95 per cent. of antimonious oxide in tartar emetic. Theory required 43.37 per cent. ($Sb=120$, $KSbOC_4H_4O_6.\frac{1}{2}H_2O=332$). The cause of this discrepancy between arsenite and tartar emetic solutions made up as standards according to the accepted molecular formulas is a matter of considerable interest. One suggested explanation of this difference has been found in the supposition that the end reaction between starch and iodine is delayed when titrating tartar emetic by iodine until an excess of iodine is present. I have already shown in a previous paper[2] that a pure starch solution gives a sharp end reaction with both tartar emetic and arsenite solutions and that while with impure starch there is a loss of iodine accompanied by the production of reddish hues in titrating tartar emetic, as shown by the difference between the readings made in the presence of potassium iodide by the yellow color of

[1] *Am. J. Sci.*, 46, 206.

[2] *Ibid.*, May, 1902, pp. 379-399.

iodine and by the blue of starch iodide, yet it is no greater than in titrating arsenite solution in the presence of an impure starch. If only an impure starch is available, the reading should be made without starch, for the presence of potassium iodide renders very sharp the yellow color of the first excess of free iodine. This first reading may be afterwards corroborated by adding the starch solution which will then give only a pure blue color. The above discrepancy must then be due to some other cause than delay of formation of the starch iodide. The present paper will prove that this discrepancy is due to the ease with which tartar emetic loses its water of crystallization and that in order to get a salt of the exact composition, $KSbOC_4H_4O_6.\frac{1}{2}H_2O$ (mol. wt. 332.15), certain conditions must be very closely observed.

In the previous paper[1] a tartar emetic solution was used containing exactly 16 grams of tartar emetic to the liter, 25 grams of tartaric acid, and 1 cc. of concentrated hydrochloric acid. Of this solution 50 cc. were oxidized by 47.75 cc. of decinormal iodine solution. Now 49.48 cc. of the iodine solution oxidized 50 cc. of a decinormal arsenite solution. Therefore it should have taken 47.68 cc. of the iodine solution to oxidize 50 cc. of the tartar emetic solution; that is to say, the tartar emetic took 0.07 cc. of decinormal iodine solution more than the theory. Calculated on the ratio of antimony to tartar emetic used the error was 0.06+ per cent. The tartar emetic was recrystallized from a boiling water solution, filtered, and air-dried. In the following experiments two different samples of commercial tartar emetic were used, which will be designated as C_1 and C_2. C_1 was in crystalline condition, containing medium-sized crystals; C_2 was in fine powdery form. Twelve different recrystallized products were used, designated as R_1, R_2, etc., to R_{12}. R_1, R_3, R_{11} and R_{12} were recrystallized from C_2, the others from C_1; R_1, R_9, R_{10}, R_{11} and R_{12} were in medium-sized crystals from $\frac{1}{32}$ to $\frac{1}{4}$ of an inch in size. By rapid stirring, R_2 and R_3 were crystallized in very fine condition. R_4, R_5, R_6, R_7 and R_8 were crystallized in exceedingly fine condition by precipitation by alcohol with rapid stirring. The attempt was made to get both a definite crystalline salt and a definite anhydrous salt.

Decinormal solutions were made as follows: Exactly 16.6075

[1] *Loc. cit.*

grams of the crystalline tartar emetic (332.15) or 16.1575 grams of the anhydrous salt (323.15) were weighed out and dissolved in a little water by the aid of a filtered solution of 25 grams of tartaric acid. This solution, upon dilution, sometimes gave a crystalline precipitate which, however, completely redissolved upon further dilution and the addition of 5 cc. of concentrated hydrochloric acid. The solution was then diluted to the liter mark. No heat was necessary in making the solutions, a thorough shaking being sufficient to dissolve the tartar emetic in the tartaric acid. The strength of the solutions was determined by decinormal iodine solutions, containing 12.685 grams of iodine and 18 grams of potassium iodide to the liter. The iodine solutions were standardized by carefully prepared decinormal arsenite solutions, containing exactly 4.95 grams of resublimed arsenious oxide, dissolved by the aid of 3 grams of pure potassium hydroxide or of 70 cc. of a saturated solution of acid potassium carbonate. For titration a few cubic centimeters of the saturated solution of acid potassium carbonate were added.

From the recrystallized salt, R_2, five different decinormal solutions were made, two in liter flasks and three in half-liter flasks.

The solutions in Table I, division *A*, were made from the freshly precipitated crystals; those in *B* after the crystals, which were in fine condition, had stood several weeks. The experiments in *A* show that the finely crystalline tartar emetic was dried just to the point at which, if made up at once into decinormal solutions, it agreed exactly with the decinormal arsenite solution. After some weeks' standing, though in a closed glass vessel, the preparation, as shown in *B*, had increased in the proportion of its antimony; that is, had lost water of crystallization.

Another recrystallization (R_3) was made from another sample of the commercial salt (C_2) and dried by exposure to the air. Decinormal solutions were made up at two different stages of the drying, and demonstrate the ease with which tartar emetic loses its water of crystallization. The crystals were exposed to sunlight for a very short time and then laid in the shade. After an hour and three-quarters the first decinormal solution was made up and titrated. The drying in the air was continued for about four hours, and a half-liter decinormal solution was made up and titrated. It is very obvious that after drying for an hour and

three-quarters the tartar emetic was not completely dry, but that after six hours' drying the fine crystals had lost some of their water of crystallization.

TABLE I.

Final volume, 125 cc. R_2 from C_1.

	N/10 tartar emetic solution.	N/10 arsenic trioxide solution.	N/10 iodine solution.	Potassium acid carbonate saturated solution.	Starch solution.	Remarks. Solution made in	Color.
	cc.	cc.	cc.	cc.	cc.		
A.	(Two solutions made from the freshly recrystallized tartar emetic.)						
(1)	..	50	49.28	5	1		medium blue (purplish)
(2)	50	..	49.28	25	1	1-liter flask	deep blue
(3)	50	..	49.29	25	1	1-liter flask	medium blue (purplish)
(4)	..	50	49.32	5	1		medium blue
(5)	50	..	49.32	25	1	1/2-liter flask	good blue
(6)	50	..	49.30	25	1	1/2-liter flask	good blue
(7)	..	50	49.31	5	1		medium blue (purplish)
B.	(Three solutions made after the crystals had stood several weeks.)						
(8)	50	..	49.60	25	1	1-liter flask	good blue
(9)	50	..	49.60	25	1	1/2-liter flask	good blue
(10)	50	..	49.58	25	1	1/2-liter flask	good blue
(11)	50	..	49.60	25	1	1/2-liter flask	good blue
(12)	50	..	49.60	25	1	1/2-liter flask	good blue

TABLE II.

Final volume, 125 cc. R_3 from C_1.

	N/10 tartar emetic solution.	N/10 iodine solution.	Potassium acid carbonate saturated solution.	Starch solution.	Air-dried. Hours.	Remarks. Solution made in	Color.
	cc.	cc.	cc.	cc.			
(13)	50	49.23	25	1	1 3/4	1-liter flask	deep blue
(14)	50	49.24	25	1			deep blue
(15)	50	49.46	25	1	6	1/2-liter flask	deep blue

For various reasons, the method of experimentation was changed to the following: Exactly 0.5 gram of tartar emetic was weighed out, dissolved in 50 cc. of water by the aid of 1 gram of tartaric acid and titrated by decinormal iodine, after the addition of 25 cc. of a saturated solution of acid potassium carbonate. The first experiments were made with two samples of recrystallized tartar emetic and with two samples of commercial tartar emetic.

TABLE III.

Final volume, 120 cc.

		Tartar emetic.	N/10 iodine solution.	Tartaric acid.	Potassium acid carbonate solution.	Starch solution.	Color.
		Gram.	cc.	Gram.	cc.	cc.	
(16)	R_1	0.5	29.82 29.85	1	25	1	faint color deep blue
(17)	R_1	0.5	29.82 29.85	1	25	1	faint color deep blue
(18)	R_1	0.5	29.82 29.85	1	25	1	faint color deep blue
(19)	R_2	0.5	29.82 29.84	1	25	1	faint color deep blue
(20)	R_2	0.5	29.88	1	25	1	very deep blue
(21)	R_2	0.5	29.84	1	25	1	medium blue
(22)	C_1	0.5	30.38	1	25	1	medium blue
(23)	C_1	0.5	30.31 30.34	1	25	1	pale purple deep blue
(24)	C_1	0.5	30.38	1	25	1	deep blue
(25)	C_2	0.5	30.38	1	25	1	deep blue
(26)	C_2	0.5	30.50 30.52	1	25	1	pale purple deep blue
(27)	C_2	0.5	30.44	1	25	1	deep blue

R_1, of medium-sized crystals, though kept for several months, agreed with the freshly recrystallized tartar emetic R_2. The two commercial samples appeared to have lost water of crystallization, or contained impurity, and C_2, which was in fine powdery condition, appeared to have lost more water than C_1, which was in medium-sized crystals. A difference in the method of commercial preparation may have been responsible for this discrepancy. That recrystallization was necessary in order to make up a standard solution was evident.

The effect of desiccators was next tried upon the recrystallized tartar emetic. A sample of R_1, finely pulverized, was placed in a desiccator containing sulphuric acid and another sample of the same preparation was put in a vacuum desiccator over sulphuric acid. The action of the two desiccators seemed to be comparable in extent and rapidity, and by comparison with experiments (16), (17), and (18) it will be seen that there is a gradual and slow loss of water of crystallization.

TABLE IV.

Final volume, 120 cc. R_1.

	In desiccator. Days.	Tartar emetic. Gram.	N/10 iodine solution. cc.	Tartaric acid. Gram.	Potassium acid carbonate solution. cc.	Starch solution. cc.	Color.
			(In sulphuric acid desiccator.)				
(28)	4	0.5	29.98	1	25	1	deep blue
(29)	7	0.5	30.01	1	25	1	deep blue
(30)	16	0.5	30.16	1	25	1	medium blue
(31)	60	0.5	30.38	1	25	1	pale blue
			(In vacuum desiccator.)				
(32)	4	0.5	29.98	1	25	1	deep blue
(33)	7	0.5	29.94	1	25	1	deep blue
		N/10 arsenic trioxide solution. cc.					
(34)	..	50	49.31	..	5	1	deep blue

The hot air-bath was then resorted to with the most varied results. Portions of R_1 and of C_1 and C_2' were heated in the air-bath. The two latter samples were taken to see whether the commercial salt could be reduced to anhydrous condition completely and agree with the recrystallized salt. The sample of R_1, in experiment (35), was heated at 120° for an hour and between 120° and 95° for three hours. The same sample was then reheated with samples of the commercial preparations and with a fresh sample of R_1 at 104°-110° for two and one-half hours, 116°-130° for two hours, and 115°-110° for three hours.

TABLE V.

		Air-bath. Hours.	Air-bath. Temperature.	Tartar emetic. Gram.	N/10 iodine solution. cc.	Tartaric acid. Gram.	Potassium acid carbonate solution. cc.	Starch solution. cc.	Color.
(35)	R_1	4	95°–120°	0.5	30.42	1	25	1	deep blue
(36)	R_1	11 1/2	95°–130°	0.5	30.41	1	25	1	deep blue
(37)	..	..	..	0.5	30.40	1	25	1	deep blue
(38)	R_1	7 1/2	104°–130°	0.5	31.10	1	25	1	deep blue
(39)	..	..	..	0.5	31.30	1	25	1	deep blue
(40)	C_1	7 1/2	104°–130°	0.5	31.00	1	25	1	medium blue (purplish)
(41)	..	..	..	0.5	30.80	1	25	1	medium blue (purplish)
(42)	C_2	7 1/2	104°–130°	0.5	30.50	1	25	1	deep blue
(43)	..	..	..	0.5	30.53	1	25	1	deep blue

The reheated sample, (36) and (37), was not changed by the second heating, but lost considerable water by the first heating. It stood in a desiccator between the two periods of heating. The fresh sample of the same preparation, (38) and (39), lost most heavily of all, and was closely followed by the more crystalline commercial sample C_1, (40) and (41), which had been powdered before heating. The finely powdered commercial sample C_2, (42) and (43), lost but little water.

The sample C_1 which had now been heated already seven and one-half hours from 104° to 130° was reheated for three hours at 160°-165°, and a fresh sample of R_1 was heated at 160°-165° for two hours. Again the fresh sample lost more water than the sample previously heated.

TABLE VI.

Final volume, 120 cc.

		Air-bath. Hours.	Air-bath. Temperature.	Tartar emetic.	N/10 iodine solution.	Tartaric acid.	Potassium acid carbonate solution.	Starch solution.	Color.
				Gram.	cc.	Gram.	cc.	cc.	
(44)	C_1	10 1/2	104°–165°	0.5	31.86	1	25	1	deep blue
(45)	..	..	..	0.5	31.70	1	25	1	deep blue
(46)	R_1	2	160°–165°	0.5	31.96	1	25	1	deep blue
(47)	..	..	..	0.5	31.91	1	25	1	deep blue

A still greater loss of water is evident in these experiments, and in this table, as well as in experiments (38) to (41) inclusive, in Table V, the discrepancy between the duplicates was due to the difficulty of weighing the portions exactly, since the dried tartar emetic took up moisture so rapidly on the balance.

In Table VII the molecular weights of tartar emetic are given, calculated from the amounts of antimony present as shown by the iodometric titration of the preceding experiments. The decinormal arsenite solution was taken as standard.

A study of the preceding tables in the light thrown upon them by Table VII leads to some interesting results. The molecular weights run in a series from that of crystalline tartar emetic down almost to the theoretical state in which the crystalline salt has lost 1.5 molecules of water, passing through all intermediate stages, but never surely resting at any one spot. Two important stages

TABLE VII.

49.29 cc. (absolute amount) of N/10 iodine solution = 50 cc. of N/10 arsenic trioxide solution.

Experiments.	N/10 tartar emetic solution.	N/10 iodine solution.	Molecular weight.	Antimony.	Remarks.
	cc.	cc.		Per cent.	
(5) and (6)	50	49.29	332.15	36.13	
(10)	50	49.56	330.34		
(8), (9), (11), (12)	50	49.58	330.21	36.35	
	Tartar emetic. Gram.				
(16) to (19), (21)	0.5	29.82	330.58		
(28) and (32)	0.5	29.95	329.13		
(29)	0.5	29.98	328.77		
(30)	0.5	30.13	327.15		
(23)	0.5	30.30	325.38		
(22), (24), and (25)	0.5	30.35	324.85		
Average (35) to (37)	0.5	30.38	324.50		
(27)	0.5	30.41	324.15		
(26), (42)	0.5	30.49	323.28		
(43)	0.5	30.51	323.15	37.14	(anhydrous)
(41)	0.5	30.77	320.34		
(40)	0.5	30.97	318.30		
(38)	0.5	31.07	317.29		
(39)	0.5	31.27	315.29		
	..		314.15		(1/2 H_2O anhydride)
(45)	0.5	31.67	311.36		
(44)	0.5	31.83	309.76		
(47)	0.5	31.88	309.28		
(46)	0.5	31.93	308.80		
	..		305.15		(H_2O anhydride—all hydroxyls gone)

are reached: when all the water of crystallization is gone, the anhydrous state, and when 0.5 molecule of water further has been lost, the first anhydride stage. The greatest error met with in the recrystallized tartar emetic, if air-dried, is about 0.2+ per cent., calculated on the ratio of antimony to tartar emetic, and that after standing in fine condition in a closed bottle for several weeks. After standing for about two weeks in a sulphuric acid desiccator the finely recrystallized tartar emetic lost almost exactly one-half of its water of crystallization, and after two months almost all of

its water of crystallization. The commercial salt (C_2) had but little water of crystallization and lost it all upon heating in the air-bath, but went no further even at the temperature of 130°. Though heated at 95°-120° for four hours, the recrystallized salt (R_1) failed to lose all of its water of crystallization, and reheating for seven and a half hours at 104°-130° failed to produce any further loss. Especially interesting are the results of heating the fresh samples at the higher temperatures. Between 120° and 130° R_1 and C_1 (in crystalline form) lost water beyond the anhydrous state and approached the anhydride ($KSbOC_4H_4O_6 - \frac{1}{2}H_2O$). Upon heating at the temperature 160°-165°, the same preparations lost yet more water and approached the state of a double anhydride in which all the hydroxyls were gone ($KSbOC_4H_4O_6 - H_2O$). The anhydride state was also indicated by the readiness of the salts, after such heating, to take up water again while on the balance. Both of these anhydrides have been previously obtained.

Liebig[1] states that, according to Dulk, Wallquist, and Brandes, and in accordance with his own experiments, tartar emetic loses its water of crystallization at 100°. By careful heating to 300° he caused tartar emetic to lose, without charring, 1 molecule of water. Dumas and Piria[2] established the fact that tartar emetic contains 0.5 molecule of water of crystallization to the accepted empirical formula. Their analyses were very close. They also heated tartar emetic to a high temperature. In an oil-bath it became brownish at 235°-240°; at 220° it was still white. They gave the following double formula: $(C_4H_4O_6)_2.(SbO)_2.K_2.H_2O$; at 100° $(C_4H_4O_6)_2.(SbO)_2.K_2$; at 220° $(C_4H_3O_6)_2.(SbO)_2.K_2$. Berlin[3] states that at 100° in a stream of dry air tartar emetic loses two-thirds of its water of crystallization very easily, but the rest with difficulty; that at a temperature slightly over 100° the body changes, losing 0.5 molecule of water at 160°-180° or by longer heating at 130°; that another half molecule of water goes at 200°-220°, making the formula now $C_4H_2O_5.SbO.K$.

A series of experiments was now made to reach the desired end by alcoholic precipitation. A concentrated, yet not saturated, solution of tartar emetic was made in boiling water and filtered into about an equal volume of 95 per cent. alcohol. The tartar

[1] *Ann. Chem.* (Liebig), **26**, 132.
[2] *Ibid.*, **44**, 85.
[3] *Ibid.*, **64**, 359.

emetic was precipitated as soon as it reached the alcohol and was frequently stirred. It was then filtered by suction, kept under suction for from five to ten minutes, and air-dried. The product was a very fine white fluffy powder. Four such recrystallizations were made at first (R_4, R_5, R_6, and R_7) and dried for different lengths of time in the air. Half-gram portions were weighed out, dissolved in 1 gram of tartaric acid, and titrated by decinormal iodine, as in the previous experiments. The results are given in Table VIII.

TABLE VIII.

		Air-dried. Hours.	Air-dried. Temperature.	Tartar emetic.	N/10 iodine solution.	Tartaric acid.	Potassium acid carbonate solution.	Starch solution.	Molecular weight.	Color.
				Gram.	cc.	Gram.	cc.	cc.		
(48)	R_4	5	25°-30°	0.5	30.09	1	25	1	328.41	medium blue
(49)	R_5	3 1/2	18°-19°	0.5	29.82	1	25	1	331.44	medium blue
(50)	R_6	2 3/4	18°-19°	0.5	29.84	1	25	1	331.20	medium blue
(51)	R_7	2 1/4	18°-19°	0.5	29.73	1	25	1	332.43	medium blue
				N/10 arsenic trioxide. cc.						
(52)	..	..	..	50	49.40	..	5	1		good blue

The iodine solution had stood unused for about a month and had grown weaker; hence the new standard was used in determining the molecular weights. The tartar emetic precipitated by alcohol, though containing water of crystallization, was in such fine condition that it lost some of its water of crystallization readily in the air, or else had been precipitated by the alcohol with an incomplete amount of water of crystallization. The influence of time upon the results of air-drying is prominent. R_5, R_6, and R_7 came, however, so near to the theory that another preparation (R_8) was made very carefully as follows:

A fairly concentrated solution of tartar emetic in 250-300 cc. of boiling water was filtered into 400 cc. of 95 per cent. alcohol, and the precipitate was filtered off by suction, washed twice by 95 per cent. alcohol, kept under good suction for fifteen minutes longer, and air-dried two and a half hours at 19°-20°. A half liter of decinormal tartar emetic solution was made up at once and titrated.

TABLE IX.

R_8.

	N/10 tartar emetic solution.	N/10 arsenic trioxide solution.	N/10 iodine solution.	Potassium acid carbonate solution.	Starch solution.	Color.
	cc.	cc.	cc.	cc.	cc.	
(53)	50	..	49.50	25	1	medium blue
(54)	50*	..	49.50	25	1	medium blue
(55)	..	50	49.40	5	1	deep blue

(56) One-half gram of the tartar emetic, dissolved in tartaric acid as above and titrated, took 29.80 cc. of decinormal iodine solution.

The agreement between the arsenic and tartar emetic standards was fairly good, but hardly close enough to warrant the use of this mode of preparing tartar emetic for standardizing purposes. As the tartar emetic in this exceedingly fine form gave uniform results and was so ready to lose its water of crystallization, it was tried in the air-bath under closely regulated conditions.

TABLE X.

		Air-bath. Hours.	Air-bath. Temperature.	Tartar emetic.	N/10 iodine solution.	Tartaric acid.	Potassium acid carbonate solution.	Starch solution.	Molecular weight.	Color.
				Gram.	cc.	Gram.	cc.	cc.		
(57)	R_4	5	94°– 99°	0.5	30.44	1	25	1	324.67	deep blue
(58)	R_5	5	94°– 99°	0.5	30.41	1	25	1		deep blue
(59)	R_6	5	94°– 99°	0.5	30.44	1	25	1	324.67	deep blue
(60)	R_7	5	94°– 99°	0.5	30.48	1	25	1		deep blue
(61)	R_4	3	96°– 99°	0.5	30.44	1	25	1	324.67	deep blue
				N/10 arsenic trioxide. cc.						
(62)	..	..	..	50	49.42	..	5	1		deep blue
				Tartar emetic. Gram.						
(63)	R_4	7	97°–103°	0.5	30.49	1	25	1		deep blue
(64)	R_5	..	..	0.5	30.47	1	25	1		deep blue
(65)	R_7	..	..	0.5	30.48	1	25	1	324.19	deep blue
(66)	R_4, R_5, R_6, R_7 (mixture)	5 7	94°– 99° 97°–103°	0.5	30.48	1	25	1	324.19	deep blue
(67)	R_6*	3	97°–103°	0.5	30.48	1	25	1	324.19	deep blue

* Stood in absolute alcohol for twenty-four hours, then was filtered and air-dried.

		Air-bath. Hours.	Air-bath. Temperature.	Tartar emetic.	N/10 iodine solution.	Tartaric acid.	Potassium acid carbonate solution.	Starch solution.	Molecular weight.	Color.
				Gram.	cc.	Gram.	cc.	cc.		
(68)	R_6*	..	..	0.5	30.28	1	25	1		deep blue
				N/10 arsenic trioxide. cc.						
(69)	..	..	..	50	49.39	..	5	1		deep blue
				Tartar emetic. Gram.						
(70)	R_4	3	103°–110°	0.5	30.43	1	25	1		deep blue
(71)	R_5	3	103°–110°	0.5	30.43	1	25	1		deep blue
(72)	R_4	7	112°–115°	0.5	30.50	1	25	1		deep blue
(73)	R_5	7	112°–115°	0.5	30.46	1	25	1		deep blue
(74)	R_4	5.5	114°–121°	0.5	30.48	1	25	1	324.19	deep blue
(75)	R_5	5.5	114°–121°	0.5	30.47	1	25	1		deep blue
(76)	R_4	6	128°–130°	0.5	30.97	1	25	1	319.06	deep blue
(77)	R_5	6	128°–130°	0.5	30.57	1	25	1	323.24	deep blue
(78)	R_4, R_5, R_6, R_7 (mixture)	12 8	94°–103° 120°	0.5	30.54	1	25	1	323.55	medium blue
(79)	R_4	8	120°	0.5	30.47	1	25	1		medium blue
				N/10 arsenic trioxide. cc.						
(80)	..	..	..	50	49.61	.	5	1		medium blue
				Tartar emetic. Gram.						
(81)	R_4	8 14	120° 115°–125°	0.5	30.70	1	25	1	323.31	deep blue
(82)	R_5	8 14	120° 115°–125°	0.5	30.57	1	25	1		deep blue
(83)	R_4, R_5, R_6, R_7 (mixture)	12 8 14	94°–103° 120° 115°–125°	0.5	30.56	1	25	1		deep blue

From three to five hours' drying at 94°-99° failed to dry the tartar emetic completely to the anhydrous state (323.15). The experiments (63) to (75), made at temperatures varying about 5° from 100° to 125°, carried the drying slightly further, but still the molecular weight of tartar emetic was a unit too high for the anhydrous condition. Experiment (68) shows the effect of absolute alcohol upon the water of crystallization in twenty-four hours. In (67) this same preparation lost in three hours in the air-bath about the same amount of water as the others in a longer time.

* Stood in absolute alcohol for twenty-four hours, then was filtered and air-dried.

In (66) the portions heated in (57) to (61) were reheated, making twelve hours of total heating. This same mixture was again reheated in (78) and (83). In (73) the tartar emetic became almost entirely anhydrous according to theory, but this temperature, 128°-130°, is on the danger line, since in the duplicate experiment, (76), the tartar emetic passed slightly beyond the anhydrous condition to that of an anhydride. Experiments (78) to (83) show the effect of long heating at 115°-125°. In (78) to (81) the portions were almost anhydrous, but the other samples fell short. The difference between the readings in experiments (81) to (83) and those of the preceding experiments was due to the use of a new decinormal iodine solution. Since in these last experiments twenty-two to thirty-four hours' drying at 115°-125° failed to bring uniform and sufficiently exact results, it is hardly possible to make up standard decinormal tartar emetic solutions from the product obtained by drying in the air-bath, and the method of precipitation by alcohol yields the most susceptible form of tartar emetic for this purpose. This conclusion is exemplified in Table XI. A decinormal solution of tartar emetic was made up in a 500 cc. flask from a mixture of the products in experiments (57) to (61) and another from the products dried at 100°-120°. These solutions were made on a basis of 323.15 (molecular weight of anhydrous tartar emetic) *i. e.*, 16.1575 grams per liter.

TABLE XI.

	Temperature of drying.	N/10 tartar emetic.	N/10 iodine solution.	Potassium acid carbonate solution.	Starch solution.	
		cc.	cc.	cc.	cc.	Color.
(84)	94°- 99°	50	49.15	25	1	medium blue
(85)	100°-120°	50	49.19	25	1	medium blue

If in experiment (84) the value of 49.15 be taken as standard, then the molecular weight for 30.41, absolute decinormal iodine value obtained for 0.5 gram of this preparation in experiments (57) to (61), is 332.08. Therefore the decinormal solution agreed with the half-gram values, but both were too low as the decinormal arsenite standard of the iodine solution was 49.40. The portion dried at 100°-120° likewise fell short of the arsenite

standard, which was made certain by two separately prepared decinormal arsenite solutions.

The effect of drying in a sulphuric acid desiccator was also tried upon the product precipitated by alcohol. The last traces of water of crystallization appear to be exceedingly difficult to drive out.

TABLE XII.

	Time in desiccator. Days.	Tartar emetic. Gram.	N/10 iodine solution. cc.	Tartaric acid. Gram.	Potassium acid carbonate solution. cc.	Starch solution. cc.	Molecular weight.	Color.
(86)	2	0.5	30.19	1	25	1		medium blue
(87)	5	0.5	30.35	1	25	1		deep blue
(88)	9	0.5	30.40	1	25	1		deep blue
(89)	18	0.5	30.46	1	25	1		medium blue
(90)	25	0.5	30.48	1	25	1	324.19	medium blue

As a last resource, the tartar emetic was recrystallized in medium-sized crystals, and air-dried. It will be remembered that the first recrystallization was made in this manner and that medium-sized crystals showed far less tendency to lose water of crystallization than the finely crystallized product. Four preparations were made up, two apiece from two commercial samples, and upon two different days. In about 300 cc. of boiling water enough tartar emetic was dissolved to make a concentrated, but not saturated, solution, which was filtered into flat crystallizing dishes and allowed to crystallize over night. The crystallization should not be too rapid. The crystals were filtered off by suction, washed twice with distilled water, and kept under suction for about five to ten minutes additional. They were then air-dried from one and a half to four hours at a room temperature of 19°-24°. The air was clear and dry. The crystals were pulverized and decinormal solutions made up in the usual manner in a half-liter flask.

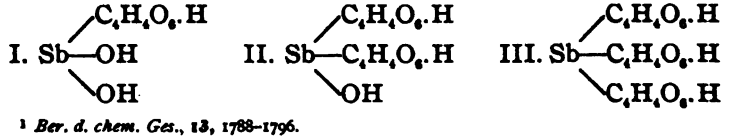
These results, as close as could reasonably be expected, are given just as they came. No inferior experiments have been omitted. It is possible, by working with care, to make up decinormal tartar emetic solutions agreeing with decinormal arsenite by recrystallizing the tartar emetic slowly in medium-sized crystals, $^1/_{32}$ to $^1/_4$ of an inch in size, washing well with distilled water,

TABLE XIII.

		Air-dried. Hours.	Air-dried. Temperature.	N/10 tartar emetic solution.	N/10 arsenic trioxide solution.	N/10 iodine solution.	Potassium acid carbonate solution.	Starch solution.	Color.
				cc.	cc.	cc.	cc.	cc.	
				(From C_1.)					
(91)	R_9	1 1/2	19°–24°	50	..	49.32	25	1	medium blue
(92)	R_9	4	19°–24°	50	..	49.42	25	1	medium blue
(93)	R_{10}	2 1/2	19°–24°	50	..	49.43	25	1	medium blue
(94)	..	..	..	..	50	49.43	5	1	medium blue
				(From C_2.)					
(95)	R_{11}	3	19°–24°	50	..	49.58	25	1	deep blue
(96)	R_{12}	4	19°–24°	50	..	49.58	25	1	medium blue
(97)	..	..	..	..	50	49.61	5	1	medium blue

removing most of the moisture by about ten minutes' good suction, and air-drying from two and a half to four hours. The crystals should not lie exposed to the air for many hours after they are dry, and for exact work should be freshly prepared. On a damp day it might take longer to dry them than the time given above, but heat should never be used. The laboratory temperature should not range above 25° and should be preferably lower. The crystals in the above preparations were considered dry when they showed not the slightest tendency to cling to a glass rod and were left exposed for an hour or two longer to make certain.

It has already been suggested that the antimony in tartar emetic is not attached to the carboxyl end of tartaric acid but to the alcoholic end. Clarke and Stallo,[1] in 1880, opposed the idea that the group (—Sb=O) existed in tartar emetic and suggested that tartar emetic was a salt of SbO_2H_3. They gave the formula $Sb\begin{cases} C_4H_4O_6 \\ OK \end{cases}$ for tartaric emetic. Clarke and Evans[2] found it difficult to obtain distinct products of tartaric acid and antimonious acid, and suggested the possible existence of a row of salts.



[1] *Ber. d. chem. Ges.*, 13, 1788–1796.
[2] *Ibid.*, 16, 2379–2387.

IV. $Sb = C_4H_4O_6$ / O / $Sb = O$

V. $Sb = C_4H_4O_6$ / $C_4H_4O_6$ / $Sb = O$

VI. $Sb = C_4H_4O_6$ / $C_4H_4O_6$ / $Sb = C_4H_4O_6$

They thought they obtained in definite condition III, V, and VI, and apparently II. They changed the earlier published formula of tartar emetic to

$$\begin{array}{c} Sb{-}C_4H_4O_6\,K \\ O\diagup\quad\diagdown O \\ Sb{-}C_4H_4O_6.K \end{array}$$

However, they make no distinct remark as to whether antimony is joined to the carboxyl or hydroxyl end of tartaric acid, but the idea of the acid function of antimony suggests the latter linking. Duve,[1] in 1869, claimed that boric acid united at the hydroxyl end of salts of tartaric acid. He believed that he separated the three following bodies:

$KCO_2{-}CH.BO_2$ / $HCO_2{-}CH.OH$

$KCO_2{-}CH.BO_2$ / $KCO_2{-}CH.OH$

$KCO_2{-}CH.BO_2$ / $KCO_2{-}CH.BO_2$

Adam[2] gives several reasons for believing that antimony plays the part of an acid and not of a base in tartar emetic. Of these the following seem to be of the greatest weight.

First. Bodies analogous to antimonious oxide react with alcoholic hydroxyls of organic bodies, *e. g.*, $C_4H_2O_6Na_2(BoO)_2$ noted by Duve, and sodium borosalicylate described by himself. Sodium lactate reacts with boric acid, with antimonious oxide, and with arsenious oxide; potassium bimalate with boric acid, and with antimonious oxide; and Rochelle salt with one or two molecules of boric acid.

Second. Only those acids which possess a phenol or alcoholic function combine with antimonious oxide, boric acid, etc. He, himself, established the fact that oxalic acid, phthalic acid, and their salts do not combine with boric acid.

Third. As a rule the free organic acid does not react with these bodies. Tartaric acid and antimonious oxide are an exception to this rule, however, as they do form unstable bodies. Klein[3] showed that boric acid combines with salts of mucic acid and of

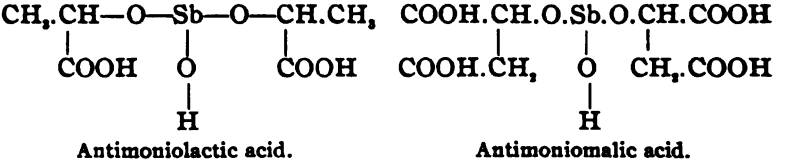
[1] *Jsb. d. Chem.* (1869), p. 540.
[2] *Compt. rend.*, 118, 1273.
[3] *Compt. rend.*, 96, 1802 and 97, 1437.

saccharic acid, but not with the free acid. He himself noted inaction between salicylic acid and boric acid.

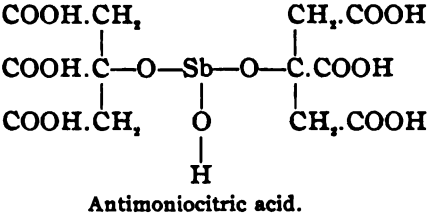
Fourth. Only organic salts or acids with a free hydroxyl group prevent the precipitation of ferric hydroxide by potassium hydroxide, *e. g.*, lactic acid, malic acid, tartaric acid, salicylic acid, but not sodium borosalicylate. Monoborotartrate also prevents precipitation.

Fifth. Upon adding alkali, acid potassium carbonate, to tartar emetic heat is given off at once, but antimonious oxide is but gradually and slowly precipitated.

Henderson and Ewing,[1] in 1895, prepared various salts of arsenious oxide and tartaric acid and studied the action of arsenious oxide and antimonious oxide on citric, malic, lactic, and mucic acids. They also came to the conclusion that the antimonyl group (—Sb=O) displaces a hydroxyl group, but thought that the bodies formed were derivatives of antimonious acid as Clarke and Stallo[2] suggested. They found that compounds of arsenious oxide or of antimonious oxide with citric acid, or with malic acid, which contain one hydroxyl group were composed of 1 atom of arsenic or of antimony to 2 molecules of the acid, that tartaric acid and mucic acid, having two and four hydroxyls respectively, combined in the ratio of 1 molecule of acid to 1 atom of antimony or of arsenic. They suggested the following formulas:

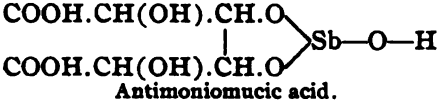


Antimoniolactic acid. Antimoniomalic acid.

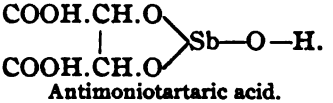


Antimoniocitric acid.

[1] *J. Chem. Soc.* (London), **67**, 102-108 and 1030-1040.
[2] *Loc. cit.*

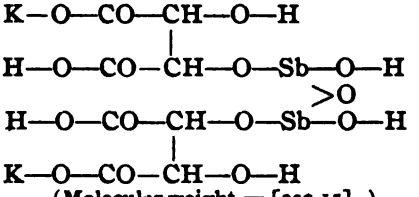


Antimoniomucic acid.



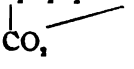
Antimoniotartaric acid.

Their last formula, applied to tartar emetic, would not, however, explain the union of that water in the compound which is ordinarily called the water of crystallization. I would suggest for crystalline tartar emetic the double formula:



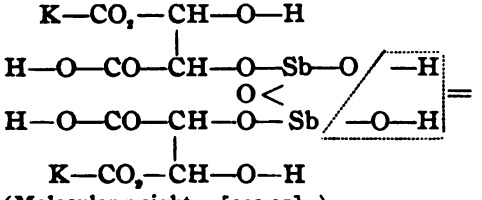
(Molecular weight $= [332.15]_2$.)

Tartaric acid forms an anhydride at 150°. The low temperature at which tartar emetic in the preceding experiments, and in accordance with the authors cited, lost 0.5 molecule of water between 130° and 160° would appear to be better explained by the formation of a tartar emetic anhydride than by a dehydration of the alcoholic groups according to the classic formula, or by such an action as Schiff,[1] represents in the formula $COOK.C_2H_2O_2=Sb.$



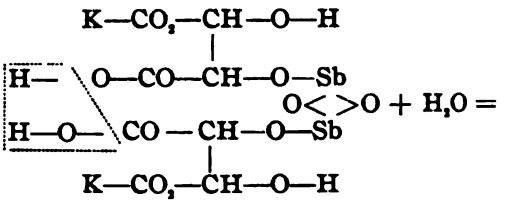
Schiff[2] calls tartaric acid tetrabasic.

The various steps of dehydration of tartar emetic from the crystalline state, according to the formula proposed, might be represented as follows:

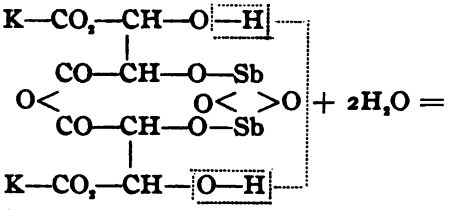


(Molecular weight $= [332.15]_2$.)
(Tartar emetic, crystalline.)

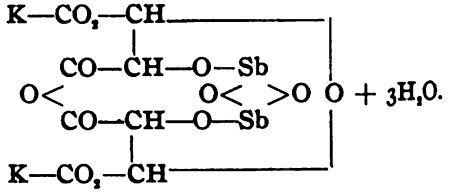
[1] Beilstein's "Handbuch," Vol. I, p. 794. line 3.
[2] *Compt. rend.*, 55, 511.



(Molecular weight = $[323.15]_2$.)
(Tartar emetic, anhydrous.)

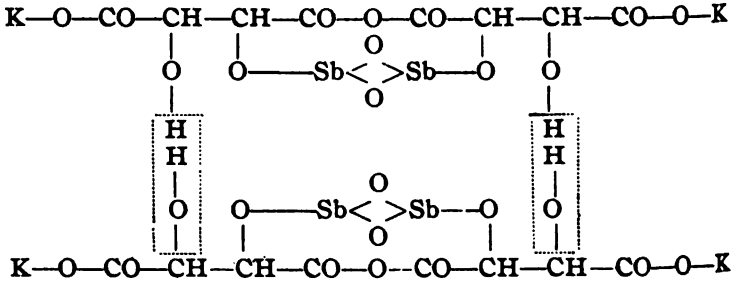


(Molecular weight = $[314.15]_2$.)
(Tartar emetic, anhydride.)

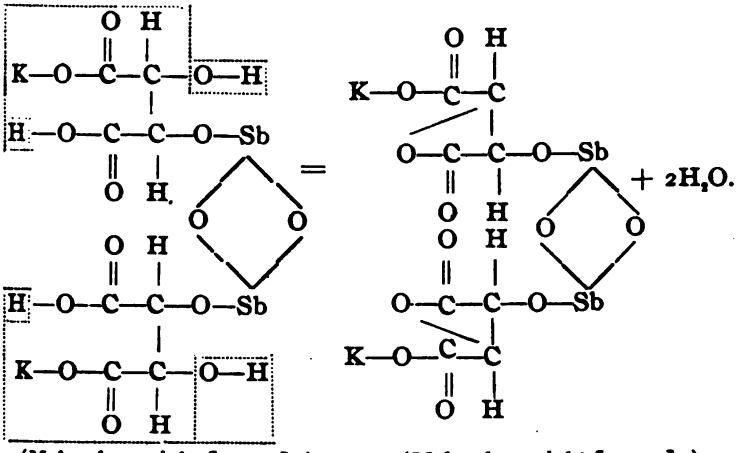


(Molecular weight = $[305.15]_2$.)
(Tartar emetic, double anhydride.)

The last reaction may be even better represented by doubling the equation and forming an anhydride between four molecules thus:



It is also possible that a lactone may form from the anhydrous salt instead of the further dehydration in steps thus:



(Molecular weight $[323.15]_2$.) (Molecular weight $[305.15]_2$.)
(Tartar emetic, anhydrous.) (Tartar emetic, lactone.)

SUMMARY.

It has been shown that the discrepancy between tartar emetic and arsenious oxide solutions lies in the ready tendency of the tartar emetic to lose its water of crystallization. If in fine crystalline or powdery form, tartar emetic loses its water of crystallization slowly in the air, more rapidly over sulphuric acid in an ordinary or vacuum desiccator, and somewhat upon standing in closed bottles; at a temperature of 128°-130°, it begins to form an anhydride losing one-half molecule of water; at 160°-165° it loses another molecule of water and becomes doubly anhydride. The formation of these anhydrides seems best explained structurally by attaching the antimony to the hydroxyl rather than to the carboxyl end of tartar emetic. If tartar emetic be recrystallized in medium-sized crystals, filtered, washed two or three times with distilled water, drained under suction for from five to ten minutes, and exposed at a temperature not exceeding 25° for a period of from three to four hours to the action of a dry atmosphere, decinormal solutions of the salt thus freshly prepared will correspond exactly to decinormal solutions of arsenious oxide.

THE KENT CHEMICAL LABORATORY
OF YALE UNIVERSITY.

PHOTOMETRIC DETERMINATION OF IRON.

By J. I. D. Hinds and Myrtis Louise Cullum.

Received May 24, 1900.

The present investigation was undertaken for the purpose of ascertaining whether the photometric method was applicable to colored precipitates.

Solutions of iron of various degrees of dilution were prepared and their strength accurately determined gravimetrically. The iron was precipitated with potassium ferrocyanide. Ferric nitrate, sulphate and chloride were found to give practically the same results. In all the solutions nitric acid was present, though never more than to the extent of 1 per cent. This was in order to insure that the iron was in the ferric condition.

As in the previous investigations,[1] a common candle was used with the simple photometric cylinder. The more accurate instrument suggested by Professor D. D. Jackson[2] was not at our command. The work was carried on in the diffused light of the laboratory, but the cylinder was protected by the hand and body against any glare of light from the windows.

Preliminary tests with the solid ferrocyanide showed that constant readings could not be obtained. The reading was found to be a function of the amount of the ferrocyanide added. This is because the ferric ferrocyanide precipitate is soluble in an excess both of the iron and ferrocyanide solutions. We therefore made a 5 per cent. solution of the potassium ferrocyanide and used it from a burette. On adding this drop by drop to a ferric solution, there first appears a blue color, then a coarse precipitate which presently breaks up into a fine state of division and finally dissolves. The greatest opacity and therefore the lowest photometric reading occurs just when the precipitate begins to break up. This point is reached when the amount of ferrocyanide bears to that of the iron present about the proportion of its molecular weight to the atomic weight of iron; or when the ferrocyanide is a little in excess of the amount necessary to convert the iron into Prussian blue. For example, a solution which contained 0.0054 gram of iron required 0.7 cc. of the 5 per cent. ferrocyanide solution, or 0.035 gram

[1] This Journal, 18, 661.

[2] *Ibid.*, 23, 799.

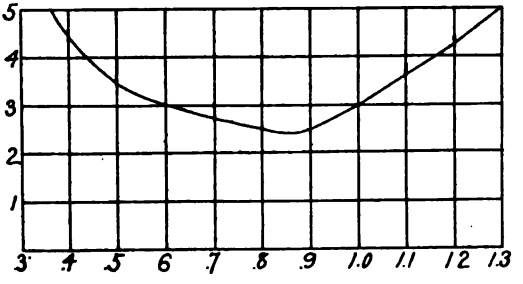
potassium ferrocyanide. These numbers are in the proportion of 54 to 350 or 56 (atomic weight of iron) to 366 (molecular weight of potassium ferrocyanide 368).

It was found that at the point of maximum opacity, or where the reading had a minimum value, constant conditions and constant readings could be obtained. The following method was then adopted: The solution whose strength was to be determined was placed in a lipped beaker in quantity sufficient to fill the photometer to the required height, and the ferrocyanide added, drop by drop, until the precipitate just appeared. The solution was thoroughly mixed by pouring back and forth, and the reading taken. Another drop of the ferrocyanide was added and another reading taken (which should be lower than the first one). This process was continued until a minimum was obtained and the readings began to rise again. The lowest reading was the one adopted.

With a little practice only four or five readings are necessary to find the minimum, which is the easier to detect because the opacity near the minimum remains nearly the same for two or three readings.

An example and diagram will illustrate the peculiar action under consideration.

	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
Ferrocyanide used....	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
	cm.	cm.	cm.	cm.	cm.	cm.	cm.	cm.	cm.
Photometer readings..	4.4	3.6	3.0	2.7	2.5	2.5	3.0	3.7	4.3



It appears that the ascending arm of the curve is nearly a straight line and rises at an angle a little higher than that of the descending arm.

A series of determinations was made and each was tested by numerous readings. In the first column of the table which follows is given the number of the solution; in the second its real strength

in per cent. of iron or grams in 100 cc.; in the third is the photometric reading; in the fourth is the product of the reading and strength; in the fifth is the strength computed from the first equation determined below; in the sixth the difference between the computed and real strength; in the seventh the strength as computed from the second equation; and in the eighth the difference between this and the real strength.

No.	Strength. y = per cent. Fe.	Reading. x.	xy.	$y=\frac{0.03027}{x-0.28}$.	Difference.	$y=\frac{0.02955}{x-0.375}$.	Difference.
1	0.01153	2.9	0.03344	0.01155	0.00002	0.01170	0.00017
2	0.00864	3.8	0.03283	0.00859	0.00005	0.00863	0.00001
3	0.00757	4.3	0.03255	0.00753	0.00004	0.00754	0.00003
4	0.00692	4.7	0.03252	0.00685	0.00007	0.00683	0.00009
5	0.00606	5.3	0.03212	0.00603	0.00003	0.00600	0.00006
6	0.00528	6.0	0.03168	0.00529	0.00001	0.00525	0.00003
7	0.00470	6.7	0.03149	0.00471	0.00001	0.00467	0.00003
8	0.00422	7.4	0.03123	0.00425	0.00003	0.00421	0.00001
9	0.00379	8.1	0.03070	0.00387	0.00008	0.00383	0.00004
10	0.00352	8.7	0.03062	0.00359	0.00007	0.00355	0.00003
11	0.00313	9.7	0.03036	0.00321	0.00008	0.00317	0.00004

Assuming the equation of the hyperbola $xy + by = a$ in which x represents the photometric reading and y the strength of the solution, and forming the observation and normal equations and solving for the constants we obtain the equation

$$y = \frac{0.03027}{x - 0.28}.$$

Twenty-two sets of observations, including readings from 1.7 cm. to 10.7 cm., were used in the computation of this equation and its efficiency may be judged by the numbers in the first column of differences in the table above.

The readings below 3 cm. and above 9 cm. were found to be rather uncertain. Rejecting these and some others which seemed to be a little inconsistent with the general series and using only the eleven found in the table, we obtain the equation

$$y = \frac{0.02955}{x - 0.375}.$$

The values computed from this equation are found in the seventh column, and in the eighth column are the differences between these values and the real strengths of the solutions. These differences run a little more regularly than those in the sixth

column, but practically one is about as good as the other. They all show that the values computed from either equation are true to the fourth decimal-place of per cent., or to parts in 1,000,000. Using the numbers from 2 to 12 for the probable error of one determination, we find, n being the number of equations, q the number of variables, and v the differences,

$$r = 0.6745\sqrt{\frac{\Sigma v^2}{n-q}} = \sqrt{\frac{0.00000000187}{10-2}} = 0.000034,$$

or three parts in 10,000,000.

This method is applicable to all mixed solutions of iron containing no metal which is precipitated with potassium ferrocyanide, such as cobalt, nickel, manganese, etc. In the analysis of phosphates and fertilizers the iron may be determined in the solution made for the determination of phosphorus. It may be necessary to dilute the solution if the iron is present in considerable quantity. The following is an example:

Amount taken: 0.3988 gram phosphate rock, which was dissolved in nitric and hydrochloric acids and made up to 200 cc.

Photometric reading was 6.5 cm., corresponding to 0.00489 per cent. iron. 200 cc. therefore contained 0.00972 gram iron. Of the 0.3988 gram rock, this is 2.45 per cent.

TABLE FOR PHOTOMETRIC DETERMINATION OF IRON.

cm. x.	Per cent. of iron. $y = \frac{0.03027}{x - 0.28}$	cm. x.	Per cent. of iron. $y = \frac{0.03027}{x - 0.28}$	cm. x.	Per cent. of iron. $y = \frac{0.03027}{x - 0.28}$
2.0	0.01759	3.8	0.00859	5.6	0.00569
2.1	0.01663	3.9	0.00836	5.7	0.00558
2.2	0.01576	4.0	0.00814	5.8	0.00548
2.3	0.01499	4.1	0.00792	5.9	0.00539
2.4	0.01428	4.2	0.00775	6.0	0.00528
2.5	0.01363	4.3	0.00753	6.1	0.00520
2.6	0.01305	4.4	0.00732	6.2	0.00511
2.7	0.01251	4.5	0.00717	6.3	0.00503
2.8	0.01201	4.6	0.00701	6.4	0.00495
2.9	0.01155	4.7	0.00685	6.5	0.00487
3.0	0.01113	4.8	0.00670	6.6	0.00479
3.1	0.01073	4.9	0.00655	6.7	0.00472
3.2	0.01036	5.0	0.00641	6.8	0.00464
3.3	0.01002	5.1	0.00628	6.9	0.00457
3.4	0.00970	5.2	0.00615	7.0	0.00450
3.5	0.00940	5.3	0.00603	7.1	0.00444
3.6	0.00910	5.4	0.00591	7.2	0.00437
3.7	0.00885	5.5	0.00579	7.3	0.00431

cm. x.	Per cent. of iron. $y=\frac{0.03027}{x-0.28}$	cm. x.	Per cent. of iron. $y=\frac{0.03027}{x-0.28}$	cm. x.	Per cent. of iron. $y=\frac{0.03027}{x-0.28}$
7.4	0.00425	8.6	0.00363	9.8	0.00318
7.5	0.00419	8.7	0.00359	9.9	0.00314
7.6	0.00414	8.8	0.00355	10.0	0.00311
7.7	0.00408	8.9	0.00351	10.1	0.00308
7.8	0.00402	9.0	0.00347	10.2	0.00305
7.9	0.00397	9.1	0.00343	10.3	0.00302
8.0	0.00392	9.2	0.00339	10.4	0.00299
8.1	0.00387	9.3	0.00335	10.5	0.00296
8.2	0.00382	9.4	0.00331	10 6	0.00293
8.3	0.00377	9.5	0.00328	10.7	0.00290
8.4	0.00372	9.6	0.00324	10.8	0.00288
8.5	0.00368	9.7	0.00321	10.9	0.00285

UNIVERSITY OF NASHVILLE,
NASHVILLE, TENN.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 68.]

ON THE DETERMINATION OF SULPHUR IN COAL.[1]

BY CHARLES W. STODDART.

Received May 26, 1900.

THE Committee on Coal Analysis, appointed by the American Chemical Society in 1895, failed to select one standard method for the estimation of sulphur in coal. The following work was undertaken with reference to this fact, and to decide, if possible, which of the many rapid determinations is the most accurate.

COALS EMPLOYED.

The coals used were selected from a large number of samples, and represent a wide range of composition and locality. The following analyses of these coals are arranged in order of hardness, from coke to lignite, with sulphur content as first found by the ordinary Eschka method:

	HH. Per cent.	FF. Per cent.	X. Per cent.	T. Per cent.
Moisture	0.00	1.93	2.22	1.10
Volatile combustible matter	0.70	2.55	3.78	4.87
Ash	10.78	1.97	6.91	16.25
Sulphur	1.03	0.73	0.80	2.02
Carbon	87.49	92.82	86.29	75.76

[1] Read at the May meeting of the New York Section of the American Chemical Society.

	AA. Per cent.	A. Per cent.	I. Per cent.	K. Per cent.
Moisture	2.25	2.22	0.48	0.34
Volatile combustible matter	4.94	7.55	15.82	17.72
Ash	3.13	14.93	3.83	6.95
Sulphur	0.58	0.91	0.61	1.20
Carbon	89.10	74.39	79.26	73.79

	H. Per cent.	P. Per cent.	L. Per cent.	N. Per cent.
Moisture	0.40	0.44	0.53	0.89
Volatile combustible matter	18.40	20.40	28.89	32.15
Ash	3.21	6.32	12.22	4.40
Sulphur	0.70	1.71	2.93	0.65
Carbon	77.29	71.13	55.43	61.91

	E. Per cent.	D. Per cent.	B. Per cent.	GG. Per cent.
Moisture	0.99	0.77	0.87	17.77
Volatile combustible matter	34.36	40.76	72.86	43.76
Ash	10.56	6.72	6.15	7.60
Sulphur	2.20	1.12	1.85	0.51
Carbon	51.89	50.63	18.27	30.36

HH is a Connellsville coke, Pennsylvania.

FF, broken coal from Luzerne County, Pennsylvania.

X, anthracite coal from Pittston, Pennsylvania.

T, egg coal from the Scranton District, Pennsylvania.

AA, from Kingston, Pennsylvania.

A, Ontario and Western coal.

I, from Somerset County, Pennsylvania.

K, West Virginia steam coal.

H, Pocahontas coal.

P, steam coal from the Beech Creek region, Pennsylvania.

L, steam coal from West Virginia.

N, high-grade steam coal from the Buffalo, Rochester, and Pittsburgh region, Pennsylvania.

E, gas coal from West Virginia.

D, gas coal from West Virginia.

B, cannel coal from Grayson, Kentucky.

GG, lignite, from Bismarck, North Dakota.

SELECTION OF METHODS.

In going over the various methods employed for the determination of sulphur in coal, it was found that the number was too great to admit of all being applied to each sample; therefore certain methods were selected as typical ones for comparison on the six-

teen coals. If only two or three coals had been chosen, it would have been feasible to apply all or most of the methods; but it was thought far better to use the few important methods on many coals which varied widely in composition and sulphur content.

Carius' decomposition of the substance with fuming nitric acid in a sealed tube is accurate, and might be applied in this case, but in using coals with a high percentage of volatile combustible matter, the pressure produced would probably shatter the tube. A modification as given by Hodgson[1] permits the tube containing 0.5 gram of sample and 15 cc. of fuming nitric acid to remain open for six hours, while being heated on a water-bath at 80°-90° C.; 5 cc. more acid is then added, the tube sealed, heated at 150° C. for from four to five hours in a furnace, opened to relieve the pressure, and reheated at 180°-200° C. for from two to four hours. The residue is filtered off and treated separately for sulphur. The filtrate is evaporated down with sodium hydroxide, the nitric acid driven out by hydrochloric acid, and dehydrated. The dry mass is taken up with water, acidified slightly with hydrochloric acid, and barium chloride added. This modification is long and tedious, and no better than other methods.

The best standard means for obtaining the sulphur content of a coal is combustion in an atmosphere of oxygen, passing the products of decomposition through some absorbent solution, and testing the residue for sulphur. Sauer's combustion method[2] is probably as well known as any, but elaborate apparatus is required, and complete decomposition of the tarry products is not easy. Other modifications, notably that of Drown,[3] are not much better.

At Columbia University there is an Atwater-Blakeslee bomb calorimeter in which coal can be burned in oxygen under any pressure up to 50 atmospheres. This gives complete combustion, and as there are appliances for passing the products of combustion through absorbent solutions, all volatile sulphur compounds, if any, can be readily recovered. The combustion is almost instantaneous, the operation very simple, and all troublesome apparatus avoided. Under these circumstances the calorimeter was selected as the means of obtaining standard figures for sulphur. The method of procedure is as follows:

[1] This Journal, 20, 883.
[2] *Zischr. anal. Chem.*, 12, 32.
[3] *Am. Chem. J.*, 2, 404; 4, 11.

Standard Method.—About 0.5 gram of coal is forced into a pellet by means of the special press which accompanies the calorimeter. The pellet is carefully weighed in a tared platinum capsule, and placed in the support which consists of a wire ring fastened to a straight rod. The latter projects through the cover of the bomb. A second rod passes through the cover, parallel to the first, but not touching it. A fine iron wire, coiled spirally in the center, is attached at each end to the parallel rods, and is in contact with the pellet of coal. The cover is now placed on the bomb which is of heavy steel, platinum-lined throughout. A heavy steel flange is set over the cover and screwed down tightly by means of a lever and clamp. A lead gasket in the cover fits over the top of the bomb so that the apparatus is hermetically sealed. In the cover is a valve with a connection for the oxygen tank, in order that the gas under a pressure of 25 atmospheres can be forced into the bomb. After closing the valve and disconnecting from the tank, the bomb is attached by the projecting rods to a row of four 16 candle-power lamps in parallel, giving a current of 2 amperes. When the circuit is closed the lamps flash for an instant. The wire is of course oxidized at once when it becomes incandescent from the current, and its melting breaks the circuit. The combustion of the coal is completed. The bomb is disconnected, and a delivery tube of fine bore is introduced into the valve. The other end of the tube is fastened to a U-tube containing hydrochloric acid and bromine water. The valve is opened slightly and the compressed oxygen bubbles through the absorbent solution. If any sulphur dioxide is present, it is thus recovered. Combustion under pressure, however, in all probability converts the sulphur all to sulphur trioxide which is condensed with the moisture on the interior of the bomb. After the gas has been exhausted, the cover is removed, and the latter, as well as the inside of the bomb, thoroughly washed out into a beaker. The residue is filtered off, washed, dried, and fused with sodium potassium carbonate. Then it is leached with water, filtered, acidified, evaporated to dryness, and dehydrated, taken up with 1.5 cc. of hydrochloric acid and 200 cc. of water, filtered, 10 cc. of barium chloride added to the warm solution, and allowed to stand over night. There is usually iron present, so precipitation should be completed in the cold, and the solution not boiled at first. The

original filtrate from the bomb washings is boiled to expel bromine, 10 cc. of barium chloride added, and the sulphur determined as barium sulphate. The sum of the sulphur obtained in the filtrate and residue is the total sulphur in the coal. With an average of 580 mg. of coal taken, the barium sulphate in the residue averaged 4.2 mg.

The soft coals press very readily into pellets, but the hard coals do not. The latter were therefore packed into the capsule as tightly as possible, and a small piece of ashless filter-paper fitted over the top to prevent scattering. The coil of wire was sunk in the coal and the ends pierced the paper. In this way complete combustion of the hard coals was obtained.

Although in some cases, especially with coke, mechanical difficulties have been encountered in getting complete combustion, this method is chemically most perfect. The oxidizable sulphur is oxidized under the most favorable possible conditions, and the residual sulphur converted to sodium sulphate by fusion; now if the precaution is taken to dehydrate the silica and to precipitate the barium sulphate under the best conditions, this seems to be the most reliable method for standard results, though perhaps too long for technical work.

Other Methods.—To compare with the standard method, Eschka's was of course chosen as being the best known method for estimating sulphur in coal. A method recommended by Stolba,[1] and unlike Eschka's, was also selected. Antony and Lucchesi[2] proposed a method that, they claimed, gave better results than Eschka's. It was apparently worth trying. Their original article proposed the precipitation of barium sulphate in a nitric acid solution. This is, of course, impracticable. Dubois[3] copies their method exactly, but substitutes hydrochloric for nitric acid. As an example of fusion methods Thomson's[4] was chosen. Hodgson[5] used sodium peroxide as an oxidizing agent, and it was decided to try his method.

The details of the various methods as used in this work are as follows:

[1] Listy Chemické, 12, 203.
[2] *Gazz. chim. ital.*, 29, 181.
[3] *Bull. Assoc. Belge des Chim.*, 13, [6], 225.
[4] *J. Soc. Chem. Ind.*, 8, 526.
[5] This Journal, 20, 886.

Eschka's Method.—Heath's modification, slightly changed:[1] 1 gram of finely powdered coal is mixed with 1 gram of magnesium oxide and 0.5 gram of sodium carbonate in a platinum dish having a capacity of 75-100 cc. A crucible may be used. The magnesium oxide should be light and porous. The dish is heated on a triangle over an alcohol lamp. The mixture is frequently stirred with a platinum wire or glass rod, and the heat applied very gradually, especially with soft coals. Towards the end, the bottom of the dish should be at a low red heat. When the carbon is all consumed, the mass is transferred to a beaker and the dish rinsed, about 50 cc. of water being used. Fifteen cc. of saturated bromine water are added and the solution boiled for five minutes. The residue is allowed to settle and the clear liquid decanted through a filter; it is boiled a second and third time with 30 cc. of water, and washed very thoroughly. The residue was not further examined. The volume of the filtrate should be about 200 cc. One and a half cc. of concentrated hydrochloric acid are added and the solution is boiled until the bromine is expelled. Now 10 cc. of 10 per cent. barium chloride solution are added to the hot solution drop by drop, and with constant stirring. It is next digested over a low flame, with occasional stirring, until the precipitate settles clear. The barium sulphate is filtered and washed, using a small ashless filter-paper, ignited and weighed.

Stolba's Method.—1 gram of finely ground coal is mixed with 1 gram of silver powder and 1 gram of potassium acid carbonate, and the whole carefully heated with frequent stirring until no dark particles remain. The mass is then transferred to a beaker with about 50 cc. of water and boiled, allowed to settle, and the clear liquid decanted through a filter. Two more portions of water, 30 cc. each, are added and the solution boiled as before. The residue is now transferred to the filter and thoroughly washed. The filtrate is acidified with 1.5 cc. of hydrochloric acid and the carbon dioxide boiled out. Ten cc. of barium chloride are added, and barium sulphate is precipitated as in Eschka's method. In most cases it is found advisable to add a few drops of ammonium acetate solution to prevent a slimy brown residue from running through the filter. It is also frequently necessary to filter the

[1] This Journal, 21, 1127.

solution more than once to obtain a clear filtrate for the precipitation of barium sulphate.

Antony and Lucchesi's Method.—1 gram of finely powdered coal, mixed with 4 grams of manganese dioxide, 1 gram of potassium permanganate, and 2 grams of sodium carbonate, is placed in a platinum crucible and covered with a layer of the same oxidizing mixture. Heat is applied very gradually at first to prevent deflagration of the contents, and is finally raised until the bottom of the crucible is just reddened. After half an hour of such heating the mass is allowed to cool and is then transferred to a beaker with about 50 cc. of water and boiled. It is now allowed to settle and the clear liquid decanted through a filter. Two more additions of 30 cc. of water each are made, and the mixture is boiled as before. The mass is finally all transferred to the filter and thoroughly washed. The filtrate is acidified, and barium sulphate precipitated. In this case two filtrations are always necessary to obtain a clear solution. The addition of ammonium acetate solution helps to a great extent. Manganese dioxide is the cause of the trouble.

Thompson's Method.—1 gram of the coal is mixed with 2 grams of sodium carbonate and gently heated until all the carbon is burned away. The mass is then fused and a little potassium nitrate added to complete the oxidation to sulphate. After the mass has cooled it is leached with water, filtered, the filtrate acidified with hydrochloric acid, and evaporated to dryness. The silica is dehydrated, the mass taken up with 1.5 cc. of hydrochloric acid and about 50 cc. of water, and filtered. The filtrate is diluted to 200 cc., and barium sulphate precipitated as usual.

Hodgson's Method.—1 gram of the coal is placed in a nickel crucible and covered with 4 grams of sodium potassium carbonate and 1 gram of solid sodium hydroxide. The crucible is covered and heat applied gently until gases are driven off. Then the heat is raised and small amounts of sodium peroxide are added until no further action occurs. Perfect fusion is now obtained with the blast-lamp. The mass is allowed to cool and is then leached thoroughly with water,—about 50 cc. It is then filtered, washed with hot water, the filtrate acidified with hydrochloric acid, evaporated to dryness, the silica dehydrated, and the dry mass taken up with hydrochloric acid and water. After filtering, the sulphur is determined as usual. Only two samples were tried by

this method. The results were low, and the method unsatisfactory.

GENERAL PRECAUTIONS.

To avoid possible contamination from gas, alcohol lamps were used throughout these experiments.

All the chemicals were carefully tested for sulphur, and the necessary correction applied, if needed. Sodium carbonate, potassium acid carbonate, hydrochloric acid, and bromine contained no sulphur. Magnesium oxide contained 0.002 per cent.; manganese dioxide, 0.004 per cent.; potassium permanganate, 0.028 per cent.; sodium hydroxide 0.015 per cent.; and sodium peroxide, 0.002 per cent.

Constant acidity was maintained in all the analyses for the precipitation of barium sulphate; namely, 1.5 cc. of concentrated hydrochloric acid to 200 cc. of solution.

It was found convenient to add the barium chloride solution from a burette. After the 200 cc. of acidified solution had been heated to boiling on an asbestos disk, the burette was brought over the beaker and 10 cc. of 10 per cent. barium chloride solution were added drop by drop, stirring all the time. The stirring was continued at intervals after the barium chloride had been added, until the barium sulphate settled clear.

RESULTS.

The results as obtained by these methods are as follows:

Coal.	Combustion method. Per cent.	Eschka's method. Per cent.	"Eschka's Dehydrated."[1] Per cent.	Stolba's method. Per cent.	Manganese dioxide method. Per cent.	Thomson's method. Per cent.
HH.....	0.67	1.03	1.01	0.89	0.67	...
FF	0.70	0.73	...	0.65	0.58	0.59
X.....	0.82	0.80	...	0.81	0.79	...
T.....	1.65	2.02	1.67	1.64	...	...
AA	0.51	0.58	0.56	0.51	0.52	...
A.....	0.67	0.91	0.70	0.62	...	...
I	0.64	0.61	...	0.60	0.60	0.55
K.....	1.21	1.20	...	1.15	...	...
H	0.70	0.70	...	0 62	...	...
P.....	1.99	1.71	...	1.75	...	...
L.....	3.09	2.93	...	3.08	...	3.08
N..... ..	0.65	0.65	...	0.65	0.64	0.67
E.....	2.23	2.20	...	2.05	...	...
D.....	1.21	1.12	...	1.07	...	...
B.....	1.35	1.85	1.35	1.34	...	...
GG.....	0.53	0.51	...	0.38	0.50	...

[1] See following paragraph.

DEHYDRATION OF SILICA IN ESCHKA'S METHOD.

In examining these results it is seen that HH, T, AA, A, and B are lower by the combustion method than by Eschka's. It was thought that the higher results might be due to silica coming down with barium sulphate. To remedy this, dehydration was tried after acidification of the filtrate. The percentages thus obtained are given in the column marked "Eschka's Dehydrated." Evidently in the case of HH it was not silica that caused a high result. The trouble seems to have been in the combustion method. HH, being a coke, had practically no moisture or volatile combustible matter, and was consequently so dry that it would not pack at all in the capsule. Complete combustion was in no trial obtained, and the sulphur was not obtained on fusing the residue.

AA was lowered only a little, but T, A, and B show that dehydration of silica is necessary in order to get accurate results. T had 16 per cent. of ash, A 15 per cent., B only 6 per cent., and AA 3 per cent. Although a high percentage of ash would be expected to give more silica to contaminate the barium sulphate, this contamination is not always confined to high ash coals. The temperature to which the substance is subjected must have something to do with the interference of silica, and as it is very difficult to keep the same temperature for all the experiments, it is better in all cases to dehydrate the silica.

BARIUM, STRONTIUM, AND CALCIUM SULPHATES IN ESCHKA'S METHOD.

P, by Eschka's method, is lower than by the combustion method. The residue was tested for barium to see if sulphur as barium sulphate might have been present, and not obtained by this treatment. None was found. Nevertheless it is interesting to know whether or not Eschka's mixture obtains sulphur contained in the coal as barium sulphate, strontium sulphate, and calcium sulphate. H was selected and separate additions of 10, 20, 30 and 40 mg. of pure barium sulphate were made. The sample thus obtained was subjected to exactly the same treatment as at first. In every case the silica was dehydrated to avoid any possible contamination.

Barium sulphate in H as first analyzed = 0.0510 gram.

	Theoretical results. Gram.	Actual results. Gram.
+10 mg. barium sulphate.....	0.0610	0.0510
+20 mg. barium sulphate.....	0.0710	0.0551
+30 mg. barium sulphate.....	0.0810	0.0559
+40 mg. barium sulphate.....	0.0910	0.0622

The same additions were made again and the mass was treated at a very much higher temperature (bright red) for about an hour after the carbon was all burned off.

	Results with high heat. Gram.
+10 mg. barium sulphate	0.0613
+20 mg. barium sulphate	0.0682
+30 mg. barium sulphate	0.0667
+40 mg. barium sulphate	0.0901

These results are irregular, but indicate that, as usually carried out, the method gives a fraction of the sulphur present as barium sulphate, and that the conversion of larger amounts is entirely dependent on the increased temperature.

Using the same sample, 10 and 40 mg. of strontium sulphate were added.

	Theoretical results. Barium sulphate. Gram.	Actual results. Barium sulphate. Gram.
+10 mg. strontium sulphate.....	0.0637	0.0620
+40 mg. strontium sulphate.....	0.1018	0.0943

Also 10 and 40 mg. of calcium sulphate were added.

	Theoretical results. Barium sulphate. Gram.	Actual results. Barium sulphate. Gram.
+10 mg. calcium sulphate.	0.0681	0.0680
+40 mg. calcium sulphate	0.1196	0.1179

Silica was dehydrated in these experiments as in the case of barium sulphate.

It is a well-known fact that when strontium sulphate and calcum sulphate are boiled with sodium carbonate they are converted to strontium carbonate, calcium carbonate, and sodium sulphate. This fact alone was depended upon to get the sulphur so combined, and therefore high heating was not employed. The results indicate that such is the case. But as only 0.5 gram of sodium carbonate is used in the Eschka method, not quite all of the strontium and calcium sulphates were converted to sodium sulphate. If a larger quantity of sodium carbonate had been added, all the sulphur would have been obtained.

SILVER POWDER IN STOLBA'S METHOD.

The presence of silver powder in Stolba's method seemed unnecessary. It certainly was not needed for the purpose of carrying sulphur in solution as silver sulphate, since no precipitate of silver chloride formed on acidifying the filtrate with hydrochloric acid. To test the necessity of its use four samples (AA, L, N, and B) were chosen and the method repeated, omitting the silver powder. The results are as follows:

	Without silver powder. Per cent.	First results. Per cent.
AA	0.53	0.51
L	3.33	3.08
N	0.60	0.65
B	1.38	1.34

With the silver powder the results agree almost exactly with the standard method; without it they do not. The silver powder is evidently very useful, but what its function is we do not know.

MANGANESE DIOXIDE IN ANTONY AND LUCCHESI'S METHOD.

Results from Antony and Lucchesi's method are very good, but its fault as a rapid means of estimating sulphur is the action of the manganese dioxide. It runs through the filter very badly, requiring at least two, and usually three, filtrations to obtain a clear solution. Even then the precipitate of barium sulphate is contaminated with manganese dioxide. The addition of a few drops of ammonium acetate solution checks, to a certain extent, the running through. Great care has to be observed in heating up the mass, else deflagration will cause loss by spattering.

DEHYDRATION IN THOMSON'S METHOD.

Thomson's method seems simple and gives fair results, but dehydration of the silica is absolutely necessary after the fusion with carbonate.

SODIUM PEROXIDE IN HODGSON'S METHOD.

Hodgson's use of sodium peroxide is no improvement over the old deflagration method of fusion with carbonate and nitrate. Sodium hydroxide contains sulphur and is hard to weigh accurately. Sodium peroxide also is impure to a slight extent, and since it is added in small portions at a time, and quickly becomes sticky, it is extremely difficult to know just how much has been put in. Worst of all, the mass glows and spits violently when the

sodium peroxide is added to the fused mixture, and great care must be exercised to prevent loss. Only two samples were tried with this method. Complete combustion was in no case obtained, constant attention was required, and the use of the blast-lamp needed at the end, thus allowing contamination from the gas flame. All in all this method is exceedingly impractical.

GENERAL COMPARISON.

Comparing all these methods of estimating sulphur with the standard, it appears that Eschka's method is the best. In order to get accurate results, however, the silica must be dehydrated. For commercial purposes the method without dehydration is satisfactory. As to ease of manipulation, Eschka's method is much better than the others. There is no deflagration or sputtering of the dry mass, providing, of course, that high heat is not applied at once, and moderate care is observed. In the manganese dioxide method the mass will splutter unless extreme care is taken. Stolba's method is almost as bad. The sodium peroxide method is worst of all. As regards ease of filtration, Eschka's method is again the best. There is no running through of the residue. Manganese dioxide always runs through, and the Stolba method gives trouble. The Eschka method gives sulphur combined as strontium sulphate and calcium sulphate, and if heated to a bright red heat will get small amounts of sulphur existing as barium sulphate.

CONCLUSION.

Attention is called to the fact that a large number of coals were selected from many samples received, in order to get the widest possible range both of composition and locality. Hence the methods were tried under all conditions in which sulphur might exist. If only a few samples had been used, and very thoroughly worked over, definite conclusions would have been quickly reached —conclusions that would hold only for those few coals. Where many and varied samples are tried, the conclusions may not be quite as definite, but such as they are they apply to all coals.

The comparison of results strongly confirms the accuracy of the standard method on all the samples of coal.

Eschka's method with the silica dehydrated is the best of the existing practical methods.

The remaining methods, though capable of accuracy in many cases, and particularly adapted to certain coals, do not by the reliability of the results or the ease of manipulation rival either the standard method or that of Eschka.

The preceding work was undertaken at the suggestion of Professor Edmund H. Miller, and for his advice and assistance throughout the course of these experiments the writer owes his most grateful thanks.

QUANTITATIVE LABORATORY,
May 20, 1902.

ON A METHOD FOR THE DETERMINATION OF VERY SMALL VAPOR-TENSIONS IN CERTAIN CIRCUMSTANCES.

BY LAUNCELOT W. ANDREWS.

Received June 7, 1902.

WHILE much has been done in recent years on the vapor-tensions of solvents, there has been but little work upon the tension of volatile substances in solution. It can not be doubted, however, that an investigation of phenomena of the class alluded to, promises interesting results if the experimental difficulties can be overcome. The method to which I would invite attention is based on a comparison of the tension of the solvent, assumed as known, with that of the substance dissolved.

If a substance, whose vapor-tension is S and molecular weight is M, evaporates freely into a volume V of air until the latter is saturated, we have for the weight of the substance evaporated, W, at constant volume,

$$W = MSV \text{ const.}, \qquad (1)$$

in which the constant depends upon the units chosen. If a second substance with vapor-tension s, molecular weight m, evaporates simultaneously into the same volume of air to saturation, its weight, w, will be

$$w = msV \text{ const.} \qquad (2)$$

Combining equations (1) and (2) and assuming all quantities as known, except s and V, we have

$$s = \frac{wMS}{mW}. \qquad (3)$$

In this expression, the magnitudes indicated by the capital letters may belong to the solvent, those indicated by small letters to the substance dissolved. The vapor-tension S would, of course, be that, not of the pure solvent but as diminished by the material in solution, according to Raoult's law.

In practice the method thus outlined may be carried out as follows: Assume, as a concrete case, that a determination of the tension of iodine in a solution of this element with potassium iodide and water is to be undertaken. The solution is weighed in a suitable vessel, and placed in a thermostat. A slow current of dry air is passed through it for a time, and it is again weighed. The loss of weight equals evaporated water plus iodine, (or $= w + W$), and titration of the solution before and after shows how much of this loss is due to evaporated iodine.

All the required data for formula (3) are therefore at hand. As yet, the method has been applied only to a study of starch iodide, of which an account will be found in the following paper. It was devised and experiments with it were begun more than two years ago, but circumstances beyond control of the present writer have delayed publication so long already that it seems undesirable to withhold preliminary notice any longer.

So far as iodine solutions are concerned, I would reserve the field for a time.

CONTRIBUTIONS TO THE STUDY OF STARCH IODIDE.

By LAUNCELOT W. ANDREWS AND HENRY MAX GOETTSCH.

Received June 7, 1909.

SINCE the discovery of the blue substance known as "starch iodide" by Stromeyer,[1] our knowledge of its properties has been enriched by numerous researches[2]. In spite, however, of the remarkably extensive literature pertaining to the subject, no consensus of opinion has been arrived at with regard to either the nature of the substance, its composition, or even some of its more important properties.

Thus, while Blondlot, Béchamp, Pohl, R. Fresenius, Duclaux, Brückner, and Küster[2] consider it to be a mixture of starch with

[1] Thorpe's Dict., Vol. III, p. 565.

[2] See bibliography at the end of this paper.

iodine, or a solution of the latter in the former, Rouvier, Payen, Fritsche, Bondonneau, P. Guichard, Sonstadt, Pellet and others hold it to be a chemical compound of starch and iodine. These authorities are nevertheless far from agreement as to the composition of the compound. They give the amount of iodine contained all the way from 3.2 per cent. as a minimum, up to 19.6 per cent. as a maximum, and present formulas varying over a correspondingly wide range.

Ostwald, in the first edition of his "Wissenschaftliche Grundlagen," holds it to be an easily dissociable compound, while in the second edition of the same book, influenced probably by Küster's recent work, he adds the modifying clause "beziehungsweise einer festen Lösung." Bernthsen[1] takes an identical view,[2] regarding starch iodide as a dissociable compound.

Mylius[3] maintains that the presence of hydriodic acid or an iodide is essential to the formation of starch iodide, to which he assigns the formula $(C_{24}H_{40}O_{20}I)_4HI$ as most probable. Seyfert, as also Tóth, disputed the presence of hydriodic acid or alkali iodide as essential to the existence of the blue compound.

EXPERIMENTAL.

It seemed best to simplify the conditions so far as possible by confining the study of the action of iodine on starch to clear solutions of the latter, in order to avoid complications arising from variations in the physical condition of the starch. Therefore, in the work described in the following pages, only such solutions were used.

The iodine employed was prepared from "chemically pure" iodine of the shops by distillation with potassium iodide in a current of steam. It was free from cyanide.

The solutions of starch were made by heating maize starch[4] with water in an autoclave. At first a few drops of chloroform were added to the solutions as a preservative, but, as this seemed to induce partial precipitation of starch after standing, this practice was discarded after the first set of experiments described below.

[1] "Organische Chemie," sixth edition, p. 307.

[2] "Sowohl die Stärkekörner, als der Stärkekleister werden von Jod intensiv blau, von Brom feuergelb gefärbt, indem lockere, additionelle *Verbindungen* entstehen."

[3] See bibliography.

[4] Washed with water, dilute hydrochloric acid, alcohol and water.

Starch Iodide Prepared in the Cold.

Series 1.—Ten grams of starch were heated to 175° with 100 cc. of water for about three hours. The solution was brownish but perfectly clear, and filtered readily. A few drops of chloroform were added, and after standing a day, part of the starch had precipitated. The solution, somewhat diluted, was well shaken with fine asbestos, when it easily filtered clear.

To determine the strength of this solution, 5 cc. were evaporated to dryness at 100° and brought to constant weight by heating in an air-bath at 105°-110°. This operation demands care, in consequence of the extraordinarily hygroscopic character of the product. Five cc. of solution yielded 0.1834 gram of starch.

This standard solution was diluted to make solutions containing respectively, 10.000, 5.000, 2.500, 1.250, and 0.625 grams per liter. To each solution was added an amount of pulverized iodine equal to the amount of starch present, and the whole was shaken by a motor (usually for about six hours), allowed to stand over night, a sample withdrawn for titration, and the remainder again shaken, etc. In the following table the amounts, in grams per liter, of iodine dissolved are shown.

TABLE I.

Concentration of starch, g. per L.....	10	5[1]	5	2.5	1.25	0.625
Concentration of iodine, g. per L:						
After 5 days.....	0.744	0.474	0.468	0.290	0.264	0.242
After 7 days.....	0.842	0.520	0.526	0.348	0.290	0.252
After 10 days.....	0.894	0.552	0.566	0.342	0.299	0.262
After 11 days.....	0.922	0.572	0.598	0.408	0.318	0.270
After 12 days.....	0.936	0.580	0.598	0.402	0.322	0.286
After 17 days.....	1.028	0.648	0.652	0.428	0.318	

If the results are plotted as a curve with the respective starch concentrations as ordinates and the final iodine concentrations (solubilities) as abscissas, practically a straight line is obtained. This line cuts the x axis at a point corresponding to the iodine concentration of 0.24 gram per liter, about, that is to say, at the point corresponding very closely with the best determinations of the solubility of iodine in water. The temperature fluctuated between 22° and 25°, 20° being only once recorded.

[1] This solution was freed from chloroform by blowing air through it before adding iodine. The figures show that the presence of traces of chloroform do not influence the solubility of the iodine.

Allowing for the solubility of the iodine in the water, we find a fairly steady relation between iodine and starch. The mean value of this relation is about 7.63 per cent., or in other words, the "starch iodide" in the solution contains about 7.1 per cent. of iodine.

Since the starch solution used in this series of experiments gave some evidence of having been heated to too high a temperature (it gave with a trace of iodine a violet instead of clear blue), we determined upon another series, in which the solutions should be made at a lower temperature. It was found that the starch dissolved completely at 144° but precipitated again on cooling, but at 152° (5 atmospheres' pressure) the solution remained clear long enough for the object in view.

Series 2.—Fifteen grams of starch were heated for two and a half hours to 152° with 130 cc. of water. The resulting colorless solution filtered readily and did not show any tendency to precipitate on cooling. It was diluted without delay to 650 cc., of which 5 cc. were evaporated as before to determine the starch. 0.1077 gram of dry starch was obtained.

From this standard solution, six others were at once made, without waiting for the result of the determination, in order to avoid the possibility of separation of starch. These contained in 200 cc., respectively, 200, 150, 100, 75, 50, and 25 cc. of standard solution, or, 21.54, 16.16, 10.78, 8.08, 5.38, 2.70 grams of starch per liter.

These solutions were shaken six hours a day for ten days with excess of iodine at 21° to 26°. They then contained no undissolved starch or starch iodide, and were filtered to remove any finely divided iodine in suspension, and titrated with N/100 sodium thiosulphate. The data so obtained are recorded in the following table.

TABLE II.

C_1. Concentration of starch, grams per liter	21.54	16.16	10.78	8.08	5.38	2.70
C. Concentration of iodine dissolved, grams per liter	1.644	1.316	0.970	0.786	0.602	0.446
$C-C_0$. Concentration of iodine corrected for solubility in water	1.376	1.048	0.702	0.518	0.334	0.178
P. Ratio of starch to iodine in percentage	6.39	6.48	6.51	6.41	6.21	6.59

The data given in the table under rubrics I and II were reduced by the formula $100\frac{C-C_w}{C_s} = P$, in which

C_s = the concentration of the starch (rubric I);

C_w = the iodine dissolved in the water alone, assumed as constant;

C = total concentration of dissolved iodine (rubric II);

P = per cent. of iodine taken up by the starch.

The numerical values of C_w and of P as calculated from the observations themselves are, respectively, 0.268 and 6.43. The former is in excellent agreement with the known solubility of iodine in water. The temperature varied between 21° and 26°. The percentage of iodine to starch found, 6.43, corresponds fairly to that required by the formula $(C_6H_{10}O_5)_{12}I$, which is 6.53.

Series 3.—The preceding experiments having established that the amount of iodine taken up by the starch is constant and independent of the concentration of the starch solution so long as the water is saturated by iodine,[1] it was decided to make a series of determinations of the distribution of iodine between starch iodide solutions and an immiscible solvent (chloroform).[2]

The starch iodide solutions (being identical with those used in the experiments of Series 2) were shaken with 10 per cent. (by volume) of carefully purified chloroform in stoppered glass cylinders, until a condition of equilibrium was attained, and were then allowed to stand for several hours, usually over night, to permit the liquids to separate completely. Five cc. of the clear supernatant blue solution were titrated with N/200 thiosulphate and the rest of it transferred to a dry cylinder and mixed as before with 10 per cent. of its volume of chloroform.

In this way, six successive distribution determinations were made on each solution with constant concentration as to starch but diminishing iodine. The temperatures did not vary more than 1° from 21° throughout the series.

[1] Küster (*Ann. Chem.* (Liebig), 360, 283) concludes that the amount of iodine absorbed by *solid* starch is wholly dependent on the concentration of the solution in contact with it.

[2] Compare Jakovkin's study of the dissociation of potassium triiodide in aqueous solution (*Ztschr. phys. Chem.*, 13, 539 (1894)).

TABLE III.

Distribution of Iodine between Starch Solution and Chloroform.

1. Extraction number.	2. *A.* Concentration of iodine in starch solution.	3. *B.* Concentration of iodine in chloroform.	4. *C.* Concentration of starch.	5. $B \div A$. Distribution coefficient between solutions.	6. $BC \div A$. Distribution of iodine chloroform to starch.
0	1.644	0.00	21.54	...	...
1	1.218	4.26	21.54	3.50	75.5
2	1.076	1.42	21.54	1.32	28.4
3	0.990	0.86	21.54	0.87	18.7
4	0.918	0.72	21.54	0.78	
5	0.890	0.28	21.54	0.31	...
6	0.858	0.32	21.54	0.37	...
0	1.316	0.00	16.16	...	
1	0.910	4.06	16.16	4.46	
2	0.780	1.30	16.16	1.67	72.1
3	0.732	0.48	16.16	0.66	27.0
4	0.682	0.50	16.16	0.73	10.5
5	0.644	0.38	16.16	0.59	...
6	0.620	0.24	16.16	0.39	...
0	0.970	0.00	10.78	...	...
1	0.616	3.54	10.78	5.74	
2	0.524	0.92	10.78	1.76	61.6
3	0.484	0.40	10.78	0.83	19.0
4	0.442	0.42	10.78	0.95	8.9
5	0.408	0.34	10.78	0.83	...
6	0.380	0.28	10.78	0.74	...
0	0.786	0.00	8.08	...	...
1	0.472	3.14	8.08	6.65	
2	0.394	0.78	8.08	1.98	53.7
3	0.348	0.46	8.08	1.32	16.0
4	0.318	0.30	8.08	0.94	10.7
5	0.290	0.28	8.08	0.97	...
6	0.276	0.14	8.08	0.50	...
0	0.608	0.00	5.38	...	...
1	0.328	2.74	5.38	8.35	
2	0.250	0.78	5.38	3.12	45.0
3	0.210	0.40	5.38	1.90	16.8
4	0.190	0.20	5.38	1.05	10.2
5	0.176	0.14	5.38	0.80	. .
6	0.158	0.18	5.38	1.14	...

1. Extraction number.	2. A. Concentration of iodine in starch solution.	3. B. Concentration of iodine in chloroform.	4. C. Concentration of starch.	5. B+A. Distribution coefficient between solutions.	6. BC+A. Distribution of iodine chloroform to starch.
0	0.446	0.00	2.70	...	...
1	0.176	2.70	2.70	15.34	41.5
2	0.122	0.54	2.70	4.42	11.9
3	0.098	0.24	2.70	2.45	5.4
4	0.86	0.12	2.70	1.40	...
5	0.72	0.14	2.70	1.94	...
6	0.66	0.06	2.70	0.91	...

All concentrations are given in grams per liter.

Inasmuch as the iodine in the chloroform was determined by difference, there is an accumulation of errors in the values found for the chloroform concentrations (column 3) for the last three extractions and in the corresponding distribution coefficients (column 5). It will be observed that there is no indication of a constant distribution coefficient between chloroform and starch solution or between chloroform and dissolved starch. The results show a more rapid removal of the iodine from the solutions containing less starch, in such a way that all the curves cross at nearly a common point, corresponding to about 5 per cent., falling between the first and second extractions.

Series 4. (*Starch Iodide Prepared by Heating*).—43.152 grams of air-dried starch, containing 38.449 grams of dry starch (maize), were introduced into a Jena glass tube with 7 grams of pure iodine and enough water to moisten the mass completely. The tube was then sealed and heated to 99° for two hours. At the end of this time the contents formed a soft mass which readily dissolved in water, leaving an insoluble residue consisting of the excess of iodine only, but containing no starch. The solution, diluted to 2 liters, was found on titration with N/100 thiosulphate, to contain 2.562 mg. "free" iodine per cubic centimeter. From this standard solution were prepared, by appropriate dilution, five others, the strength of each of which, expressed in grams per liter and also in molecular volume, is shown in the following table. In calculating the latter the molecular weight of

starch is arbitrarily assumed as that of the molecule $(C_6H_{10}O_5)_6 = 972.5$.

TABLE IV.

Solution No.	Starch, grams per liter.	Iodine, grams per liter.	Molecular volume of starch.	Molecular volume of iodine.
1	19.225	2.562	50.69	99.02
2	14.42	1.922	67.58	132.03
3	9.61	1.281	101.38	198.04
4	7.21	0.961	135.16	264.06
5	4.806	0.641	202.76	396.08
6	2.403	0.320	405.52	792.16

It is obvious that these solutions prepared by the action of iodine on starch at about 100° are entirely different in composition from those previously described, which were made at about 20° from dissolved starch. The former correspond very closely with the formula $(C_6H_{10}O_5)_{12}.I_2$, whereas we have seen that the latter possesses a composition nearly agreeing with the formula $(C_6H_{10}O_5)_{12}.I$.

The solutions were shaken with chloroform repeatedly, exactly as described on a previous page. Unfortunately the temperatures were not kept constant during the extractions, and the figures show that the results were influenced by this circumstance to a much greater degree than was anticipated. It is nevertheless thought worth while to record the data obtained, since they demonstrate that in spite of the difference in percentage of iodine in the starch iodide as prepared cold and hot respectively, yet the behavior of both kinds toward an immiscible solvent is similar.

TABLE V.

1. Extraction number.	2. A. Iodine in starch solution.	3. B. Iodine in chloroform.	4. C. Concentration of starch = C.	5. $B \div A$. Distribution coefficient between solutions.	6. $BC \div A$.	7. Temperature.
0	2.562		19.22			
1	1.960	6.016	19.22	3.06	58.9	25°
2	1.816	1.450	19.22	0.80	15.4	21°
3	1.792	0.234	19.22	0.13	2.5	18°
4	1.740	0.514	19.22	0.29	5.6	19°
5	1.684	0.562	19.22	0.33	6.3	18.5°

1. Extraction number.	2. *A.* Iodine in starch solution.	3. *B.* Iodine in chloroform.	4. *C.* Concentration of starch = C.	5. *B*÷*A.* Distribution coefficient between solutions.	6. *BC*÷*A.*	7. Temperature.
0	1.922		14.42			
1	1.414	5.068	14.42	3.58	51.6	25°
2	1.308	1.068	14.42	0.82	11.7	21°
3	1.290	0.172	14.42	0.13	1.9	18°
4	1.244	0.460	14.42	0.37	5.4	19°
5	1.212	0.328	14.42	0.27	3.9	18.5°
0	1.281		9.61			
1	0.904	3.782	9.61	4.45	42.8	25°
2	0.824	0.796	9.61	0.96	9.2	21°
3	0.804	0.196	9.61	0.24	2.3	18°
4	0.778	0.262	9.61	0.34	3.3	19°
5	0.756	0.220	9.61	0.29	2.8	18.5°
0	0.961		7.206			
1	0.650	3.102	7.206	4.77	34.4	25°
2	0.594	0.562	7.206	0.95	6.7	21°
3	0.582	0.118	7.206	0.20	1.4	18°
4	0.554	0.284	7.206	0.51	3.7	19°
5	0.546	0.090	7.206	0.16	1.2	18.5°
0	0.641		4.805			
1	0.416	2.240	4.805	5.38	25.9	25°
2	0.370	0.460	4.805	1.24	6.0	21°
3	0.358	0.120	4.805	0.33	1.6	18°
4	0.336	0.222	4.805	0.66	3.2	19°
5	0.322	0.142	4.805	0.44	2.1	18.5°
0	0.320		2.403			
1	0.188	1.32	2.403	7.02	16.8	25°
2	0.160	0.286	2.403	1.79	4.3	21°
3	0.152	0.078	2.403	0.51	1.2	18°
4	0.136	0.152	2.403	1.12	2.7	19°
5	0.132	0.050	2.403	0.38	0.9	18.5°

Series 5.—More significant than the last experiments and freer from sources of error, are a number of determinations of the vapor-tension of the iodine in solutions of starch iodide, carried out after the method described by one of us in the preceding paper.

A solution was used for this purpose which contained 19.224 grams of dry starch and 1.485 grams of "free" iodine per liter, and which was prepared after the method already described by

heating the constituents together to 99°. The liquid was placed in a gas-washing apparatus, immersed in a tank of water, and a slow current of dried air was aspirated through it and then through a second similar apparatus identically charged. The object of the second vessel is to serve as control, its constancy of weight demonstrating that the current of air was slow enough to be fully saturated with the vapors of both water and iodine at the prevailing tension. In practice, small losses in the weight of this vessel were disregarded, a special experiment having shown that the ratio between iodine and water evaporated is the same when the air is *nearly* (95 per cent.) saturated as when it is fully so.

The total amount of water plus iodine evaporated during each period is given by the loss in weight of the bulb. The amount of iodine evaporated is determined by titration of the solution by N/100 thiosulphate at the close of each period of evaporation, and the water estimated by difference. The data of one such series of measurements are reproduced in Table VI. The tension in millimeters (s) of the iodine is found by the formula

$s = 0.071 \times \frac{wS}{W}$ (see preceding paper), in which

S = the tension of water-vapor at the prevailing temperature, and

w = the weight of water evaporated, and

W = the weight of iodine evaporated.

To secure greater accuracy, for each titration about 5 cc. of the solution were withdrawn and its weight determined. The iodine concentrations are accordingly given in milligrams per gram.

The minuteness of the tension of the iodine (less than 0.01 mm.) in solutions where the iodine forms 5 per cent. of the weight of the starch present is remarkable. To obtain correspondingly low tensions of iodine in solutions of potassium iodide, the amount of iodine must be reduced relatively to a much greater degree, but the general character of the curve is very similar. We have not as yet been able to calculate any satisfactory dissociation constant from the data. All the results obtained, both by the vapor-tension method and by the chloroform method, show the complexity of the phenomena involved, and lead to the hypothesis that the iodine in "starch iodide" solutions exists in two forms of union at least, a small portion of it being much more readily removed than the rest.

TABLE VI.

Table Showing Relative Evaporation of Water and of Iodine from Solutions of "Starch Iodide."

Period	1	2	3	4	5	6	7	8	9
Date	May 16	May 16	May 17	May 17	May 17	17–18	18	18–19	19-21
Time in minutes	5	10	30	150	150	960	420	1290	1800
Mean temperature	22.66°	22.63°	21.89°	21.79°	21.69°	21.00°	20.30°	19.46°	18.40°
Initial weight of solution	179.058	164.960	159.805	154.435	149.147	143.930	138.151	132.701	126.416
Final weight of solution	179.050	164.905	159.532	154.318	149.023	143.243	137.777	131.546	124.903
Loss in grams by evaporation $= w + W$	0.008	0.055	0.273	0.117	0.124	0.687	0.374	1.155	1.513
Mean concentration in milligrams of iodine per gram	1.4427	1.4190	1.3331	1.2418	1.2042	1.1303	1.0486	1.0027	0.9566
Iodine evaporated in milligrams $= w$	2.25	5.73	22.30	7.10	4.76	17.58	6.70	7.47	7.07
Water evaporated in milligrams $= W$	5.75	49.3	251	110	119	669	367	1148	1506
Tension of water-vapor $= S$	20.46	20.43	19.53	19.41	19.29	18.50	17.72	16.82	15.75
Tension of iodine-vapor $= s$	0.57	0.168	0.123	0.089	0.055	0.035	0.023	0.0078	0.0053

$$s = 0.071 \times \frac{wS}{W} = \text{tension in millimeters.}$$

The differences between the composition of the starch iodide prepared cold and that made by the aid of heat, invite a further examination of the action of high temperatures on this substance. The authorities disagree radically as to the phenomena resulting from the action of heat on solutions of this kind, some maintaining while others deny the permanent decolorization by heat when volatilization of iodine is prevented. We accordingly undertook an investigation of this matter.

Series 6.—A somewhat dilute solution of starch iodide sealed up in a tube of Jena glass and heated to 100° becomes colorless if very dilute, or straw color if less so. The color returns in its original intensity (colorimetric determination) if the tube is small and is rapidly heated to the required temperature and quickly cooled. But if the heating is continued, the color returns on cooling with ever feebler intensity, and at last fails to return at all. Seventy cc. of a solution of starch iodide (prepared like those referred to in Table V) were sealed in a Jena glass tube and heated in a steam-bath for several days, eight to ten hours each day. The solution did not lose its blue color at first (being too concentrated to do so) but the upper part of the tube showed the violet vapor of iodine. After four days the violet vapor had disappeared and the solution had become green. After heating fifty hours, the solution had become light yellow and the operation was discontinued. No pressure was apparent on opening the tube.

The solution was filtered from an insignificant greenish sediment. It was pale yellow, and gave the following reactions: Shaken with chloroform the latter becomes violet and the solution colorless. Starch paste turns it blue. Hence, free iodine is present and starch[1] is absent. Iodine dissolved very copiously in it, giving a dark brown solution. Methyl orange indicated a strongly acid reaction. Potassium nitrite set free a considerable quantity of iodine; hence, hydriodic acid is present. Mercurous nitrate gave a greenish precipitate of mercurous iodide. The solution reduced Fehling's solution, and on boiling with phenylhydrazine and acetic acid gave the crystalline precipitate characteristic of glucose.

For the purpose of quantitative study of these products, another

[1] Consequently the statement of Stocks (*Chem. News*, 87, 183), that starch is unaltered on heating with iodine in a sealed tube, is incorrect.

portion of the material was sealed up and heated as before. The changes of color observed are noted below.

After heating five hours the color while hot was dark blue.

After heating fifteen hours the color while hot was black.

After heating twenty-five hours the color while hot was very dark green.

After heating thirty-five hours the color while hot was paler green.

After heating forty-five hours the color while hot was apple-green.

After heating fifty-five hours the color while hot and cold was yellow.

After heating sixty-five hours the color while hot and cold was colorless.

The product gave the same reactions as those described for the portion heated fifty hours, excepting the reactions of free iodine. Five cc. of the solution, titrated with N/100 potassium hydroxide and methyl orange, required 1.22 cc., which corresponds to 1.55 mg. of hydriodic acid. As the solution had previously been ascertained, by titration with thiosulphate, to contain in 5 cc. 12.81 mg. of iodine, it follows that 12.12 per cent. of the iodine originally present had, by continued heating, been converted into hydriodic acid.

Another portion of 5 cc. was neutralized with calcium carbonate and titrated with standard silver solution, using potassium chromate as indicator. We found thus in the 5 cc., 13.31 mg. of iodine. It follows that the greater part of the iodine is present in the form of a colorless organic iodide which gives up the whole of its iodine readily in the cold to a silver nitrate solution. The discrepancy between the 13.31 mg. found by the silver solution and the 12.81 mg. found by thiosulphate, is not due to experimental error, but is explained by the fact that solutions of starch iodide which have been made by heating for the normal period of about two hours contain a certain amount of the colorless organic iodide —an amount which one of us has found to average between three and four per cent. of the total iodine present. The organic iodide can not be removed even in traces from the solution which has been heated sixty-five hours, by shaking it with chloroform subsequent to neutralization. The existence of a colorless organic

iodide has been assumed, but not demonstrated, by Bondonneau,[1] by Duroy,[2] and by Guichard,[3] although the last mentioned certainly came very near a demonstration by showing that starch iodide solutions, which have lost all color by evaporation of iodine, may be turned blue again by adding nitric acid, even when the hydriodic acid has (presumably) been removed by desiccation.

An important factor in the decolorization of starch iodide by prolonged heating is doubtless to be found in the saccharification of the starch by the hydriodic acid formed. That this is, however, not an essential factor was demonstrated by heating starch iodide with a small quantity of calcium carbonate in a glass tube. The heating had to be continued 110 hours to produce complete decolorization, whereas without the carbonate, under otherwise identical conditions, sixty-five hours sufficed. If starch iodide solutions are boiled in the open air until fully colorless, the resulting solution contains starch, hydriodic acid, colorless organic iodide, and glucose. Its color may be restored by addition of iodine or of iodate or of nitrous acid, etc.

While we are conscious that the question as to whether the substance called starch iodide is a compound or a solution of iodine in starch is still unsettled, we still believe that the observations recorded in this paper are more reconcilable with the former view than with the latter. If the blue color is due to the formation of a mere solution of iodine in starch, it is difficult to understand why iodine can not color dry starch blue, but the fact is that perfectly dry iodine imparts to perfectly dry starch a brownish color which becomes blue on contact with a trace of water. The presence of an organic solvent does not alter this phenomenon.

If the blue substance formed in presence of water is a mere solution of iodine in starch, what, we would like to ask, is the brown substance formed when iodine dissolves in starch in absence of water?

Potassium iodide, as is well known, in large excess imparts a brownish violet color to starch iodide solutions, dilution with water restoring the blue. As Mylius has observed, iodic acid changes the blue of starch iodide to brown, a fact which he uses to support the view that iodides must be present as an essential

[1] *Bull. Soc. Chim.*, **28**, 452 (1877).
[2] *Compt. rend.*, **51**, 1031 (1860); see also *Chem. News*, **3**, 16.
[3] *Bull. Soc. Chim.*, **3**, 115 (1863).

part of the starch-blue. On this theory the change of color is simply caused by the removal of all iodide by the iodic acid. We have, however, found that if to the brown solution so formed, sodium or potassium bicarbonate or other weakly alkaline substances be added, the blue is immediately restored. This is inexplicable on the theory alluded to, but is easily understood if the possibility of iodine acting as a base is borne in mind, a possibility which has of late been shown by other authors[1] to be a probability. This involves the supposition that the iodic acid removes the iodine from the starch iodide in the form of iodine iodate,[2] and that when a stronger base is added, the weaker one ($\overset{+}{\text{iodine}}$) is displaced and placed at the disposition of the starch once more.

SUMMARY.

Clear starch solutions made at a temperature of about 150° take up in the cold an amount of iodine corresponding to the formula $(C_6H_{10}O_5)_{12}I$. Starch heated with excess of iodine to 100° for a short time takes up an amount of iodine corresponding to the formula $(C_6H_{10}O_5)_{12}I_2$. Starch and iodine heated to 100° for a longer time give ultimately a colorless solution which contains most of the iodine in the form of an organic iodide, a smaller part of it in the form of hydriodic acid, and which also contains glucose but no starch.

Solutions of starch iodide on shaking with chloroform yield, at first, considerable amounts of iodine to the latter but after removal of the first portion, give up iodine very slowly, showing no indication of a distribution coefficient of iodine between starch and chloroform as might be expected if the iodine were merely dissolved in the starch. The vapor-tension of iodine in solutions of starch iodide was determined by a new method, and was found to be extremely minute after the removal of the first portion of the iodine.

It is held that the substance known as starch iodide is to be

[1] Compare also for a similar assumption applied to chlorine, Noyes and Lyon: This Journal, 23, 463.

[2] The process imagined may be represented by ionic equations as follows, the symbol SS standing for the starch complex.:

$$SSI + \overset{+}{H} + \overset{-}{IO_3} = SSH + \overset{+}{I} + \overset{-}{IO_3}$$

$$H_2O + \overset{+}{I} + \overset{-}{IO_3} = IOH + \overset{+}{H} + \overset{-}{IO_3}$$

$$SSH + \overset{-}{IO} + \overset{++}{2K} + \overset{-}{IO_3} = SSI + \overset{+}{2K} + \overset{-}{IO_3} + \overset{-}{OH}$$

looked upon as a dissociable additive compound of iodine with starch molecules, more or less depolymerized, according to the temperature employed, and subject therefore to variation in the ratio of starch to iodine. These views are supported by the following considerations:

1. Starch and iodine can not unite to produce the blue substance in the absence of water, a phenomenon frequently characteristic of chemical combination but not of solution in organic solvents.

2. The temporary decolorization of the blue solution by heat when loss of iodine is prevented is much better explained as a phenomenon of dissociation than of solution.

3. The fact that in the system, starch, water, chloroform, a rise of temperature has a very powerful effect in causing iodine to pass from the starch to the chloroform, indicates that the union of starch and iodine is exothermic, and agrees well with the hypothesis of a dissociable compound.

4. The fact that the amount of iodine taken up by the starch under different conditions, as to the temperature to which the starch is subjected either before or after iodine is added is naturally explained by the view that the molecule undergoes gradual depolymerization by steps, giving rise to two, or a series, of starch iodides of different composition. This also explains why no dissociation constant can be deduced.

5. The remarkably low vapor tensions of the iodine in these solutions, while quite natural if the iodine is combined, are exceptional and difficult to understand on any other basis.

The experimental part of this investigation was completed as here presented, two years ago, but publication was delayed by the temporary accidental loss of the records.

The authorities consulted (part of them it is proper to state by abstracts) are given in the following list, which is as complete a bibliography of the literature of starch iodide as we have been able to compile with the library facilities available.

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A THERMOCHEMICAL CONSTANT.

PRELIMINARY NOTICE.

By F. W. Clarke.

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It is well understood by all who have closely considered the subject, that the so-called "heats of formation" of chemical compounds are not true physical constants, but complexes of various factors. Take for example the "heat of formation" of hydriodic acid, which, according to Thomsen, has the value of —610 small calories, when calculated from gaseous iodine. This quantity, however, is only the algebraic sum of at least three quantities, one plus and two minus, as the following equation shows:

$$H_2 + I_2 = 2HI - 610 \times 2 \text{ cal.}$$

That is, heat is expended in decomposing the molecules of hydrogen and iodine, and liberated by the subsequent union of the separated atoms, the sum of the three factors being negative. The entire series of changes is endothermic; but the final step, the combination of hydrogen and iodine, must be an exothermic operation.

In most cases, thermochemical data are even more complex than in this instance, for they involve factors representing changes of physical state. The "heat of formation" of carbon dioxide, for instance, implies the gasification of carbon, the dissociation of carbon and oxygen molecules, and the actual energy of union; it is, therefore, as ordinarily determined, no true measure of chemical force. These distinct factors are not, as yet, separately measurable; their sum is difficult to interpret; and to many chemists, therefore, the complexity of thermochemistry has seemed to be hopeless. No general conclusions of unimpeachable validity have been developed from thermochemical research, and so the entire subject has fallen somewhat into disfavor. One constant alone has attracted wide-spread attention—the neutralization constant of acids by bases—and this, having a value of 13,700 calories, represents the union of hydroxyl and hydrogen ions to form water. This constant has strengthened the theory of electrolytic dissociation, and I hope now to show that it has still wider significance.

In the fourth volume of his classical "Thermochemische Unter-

suchungen," Thomsen gives data relative to the heat of combustion of 120 organic substances. These data have peculiar value, for the reason that they are strictly comparable throughout. Every substance burned was taken in the state of gas, at constant pressure, reduced to a uniform temperature of 18°, the products of combustion being gaseous carbon dioxide and *liquid* water. Upon careful scrutiny the results exhibit systematic regularities of homologous character, and this fact, which is elaborately considered by Thomsen, tends to establish confidence in the accuracy of his data. Other observers, doubtless, have done their work equally well, but no other body of measurements known to me is so homogeneous and so self-consistent as these.

In discussing his observations, Thomsen uses the so-called "heat of formation" of carbon dioxide from solid, amorphous carbon, and that of water with the latter reckoned as liquid. With these values he computes the "heat of formation" of the different substances studied, but always upon the supposition that the reactions start from the several elements in their normal molecular condition. These heats are evidently not absolute, for they involve the uncertain factors due to changes of physical state, and are therefore, as I have already shown, complexes rather than constants. Furthermore, much of Thomsen's reasoning depends upon hypotheses which have been more or less questioned, so that although his conclusions are most interesting, they have not found universal acceptance. Many important and striking relations are shown, but their significance is not fully established.

In one respect, Thomsen's data are imperfectly suited to discussion. Although he starts with gas and ends partly with gas, his water is reckoned as liquid. For the best consideration, the process of combustion should deal with gases throughout, both for substance and for products; then only can extraneous physical disturbances be practically eliminated, and the chemical part of the phenomenon be studied with the fewest complications. Fortunately, the obvious correction can be easily applied, at least approximately, and when that is done a new order of regularities appears.

According to Thomsen[1] the molecular heat of formation of liquid water from its elements at 18°, is 68,357 calories. For gaseous water the value varies with temperature, and may be represented at 100° by the quantity 58,069. At 18°—the standard

[1] Vol. II, pp. 52 to 56.

temperature of the combustion experiments—this figure reduces to 57,934. The difference between gaseous and liquid water, then, is 10,423 calories, and this quantity should be subtracted from the heat of combustion of any organic substance as many times as there are molecules of water produced. Thus, for the heat of combustion of methane, CH_4, Thomsen gives 211,930 calories. Two molecules of water are formed; we subtract, therefore, twice 10,423, and the value for gaseous substances throughout becomes 191,084. One gram-molecule of methane burning as gas, and with all the products of combustion reckoned as gaseous, gives 191,084 calories. In this way I have adjusted Thomsen's data, and in their new form they become the basis of my own calculations.

With values thus reduced we can now write equations which shall represent in thermochemical terms the process of combustion of any organic substance which, upon burning, undergoes complete dissociation. Any hydrocarbon, for example, when burning to form carbon dioxide and water, must have its atoms completely torn apart before they can combine with similarly dissociated atoms of oxygen. Let x represent the *absolute* molecular heat of formation of CO_2; y the absolute heat of formation of water; z the heat lost by the dissociation of the oxygen molecule; and r the heat lost by the decomposition of the substance burned; then, for CH_4, the equation becomes

$$x + 2y - 2z - r = 191{,}084.$$

This is a simple case; in other instances the equations must be doubled, or, in the study of organic halides and nitrogen compounds, quadrupled in order to avoid fractional molecules of oxygen, of nitrogen, or of the halogen element. For the sake of uniformity I prefer to write quadrupled equations throughout, and then the formula for the combustion of methane is

$$4x + 8y - 8z - 4r = 764{,}336.$$

Unfortunately, equations of this kind are indeterminate, for every new formula introduces a new quantity, and so the unknowns are always in excess. A direct algebraic solution is therefore impossible, and at first sight it would seem as though the entire system of equations was valueless. That this impression is incorrect I shall endeavor to show. Upon careful examination the equations exhibit regularities which suggest hypotheses; upon the

latter, trials can be based, and in that way values are discoverable which satisfy the equations in a fairly conclusive manner.

By long study of this kind I have arrived at a general formula of curious significance, at least as regards the aliphatic hydrocarbons and their non-oxygenated derivatives. Let K represent the heat of combustion for any one of these hydrocarbons; then in the quadrupled formula $4K$ must be taken. Now let a be the number of molecules of CO_2 produced; b the number of molecules of H_2O; c the number of oxygen molecules dissociated; and n the number of atomic unions or linkings in the compound burned. Then, taking these data directly from the quadrupled equation, we have the following expression:

$$\frac{4K}{12a + 6b - c - 8n} = \text{a constant.}$$

The two plus quantities in the divisor represent combinations; the two minus quantities stand for decompositions; all the terms of the fundamental equation are thus utilized. For methane, as shown in the quadrupled equation, $4K = 764{,}336$, $a = 4$, $b = 8$, $c = 8$, and $n = 4$, the last figure representing the four unions of hydrogen atoms with carbon. In ethane $n = 7$, in propane 10, etc., all linkings, whether of hydrogen with carbon, or carbon with carbon, being equal in value. Now $(12 \times 4) + (6 \times 8) - (8 \times 1) - (8 \times 4) = 56$—the divisor in the case of methane. The quotient obtained is 13,649, and this I have indicated as a constant. In the following table for fourteen aliphatic hydrocar-

Compound.	Formula.	$4K$. H_2O as liquid.	H_2O as gas.	Divisor.	Quotient.
Methane	CH_4	847720	764336	56	13649
Ethane	C_2H_6	1481760	1356684	98	13844
Propane	C_3H_8	2116848	1950080	140	13929
Trimethyl methane	C_4H_{10}	2748760	2540300	182	13957
Tetramethyl methane	C_5H_{12}	3388440	3138288	224	14010
Diisopropyl	C_6H_{14}	3996800	3704956	266	13928
Ethylene	C_2H_4	1333400	1250016	92	13587
Propylene	C_3H_6	1970960	1845884	134	13776
Isobutylene	C_4H_8	2602480	2435712	176	13839
Isoamylene	C_5H_{10}	3230520	3022060	218	13862
Acetylene	C_2H_2	1240200	1198508	86	13936
Allylene	C_3H_4	1870200	1786816	128	13959
Diallyl	C_6H_{10}	3731280	3522820	254	13869
Dipropargyl	C_6H_6	3531520	3406444	242	14076
				Average,	13873

bons its constant character appears. All the computations rest upon Thomsen's determinations, adjusted in the manner which I have described. In fixing the value of n, actual unions only are counted; double or triple carbon bonds reckon as one alone, the extra bonds being in abeyance, and thermally inoperative. In C_2H_2 for instance, $n = 3$; in ethylene, $n = 5$; in dipropargyl $n = 11$. n, therefore, for all chain molecules, equals the number of atoms in the compound minus one.

To trimethylene, if it be regarded as a ring-compound with nine unions in the molecule, the formula does not apply. The aromatic hydrocarbons also demand separate examination, and the formula for them must be modified by the introduction of a constant factor which represents the strength of the carbon ring. Since these special cases will be considered in my complete memoir later, their discussion may be omitted here.

The organic halides, sulphides and nitrogen compounds are well covered by the general formula, provided that in each case an appropriate factor be added to the divisor to indicate the halogen, sulphur dioxide or nitrogen produced upon combustion. Thus, for complete combustion of the halides, when halogen molecules are formed, the modification of the formula is as follows. Let h represent the number of chlorine molecules produced, h_1 the bromine molecules, and h_2 the iodine; then

$$\underset{\text{Chlorides.}}{\frac{4K}{12a + 6b + h - c - 8n}} = \underset{\text{Bromides.}}{\frac{4K}{12a + 6b + 2h_1 - c - 8n}} =$$

$$\underset{\text{Iodides.}}{\frac{4K}{12a + 6b + 4h_2 - c - 8n}} = \text{const.}$$

Thomsen gives data for twenty-two of these compounds, and only three of them are exceptional. Chlorobenzene, carbonyl chloride, and carbon tetrachloride fail to yield the usual constant, and their consideration is therefore deferred. The remaining nineteen compounds are given in the first of the following tables.

In dealing with the organic compounds of nitrogen, the same fundamental formula seems to hold, only it becomes necessary to divide the available data into two groups in which the factor for nitrogen has two distinct values. In the nitriles and cyanides when m represents the number of molecules of nitrogen set free,

Compound.	Formula.	4K. H_2O as liquid.	4K. H_2O as gas.	Divisor.	Quotient.
Methyl chloride	CH_3Cl	707800	645262	47	13729
Ethyl chloride	C_2H_5Cl	1336440	1232210	89	13845
Propyl chloride	C_3H_7Cl	1969520	1823598	131	13921
Isobutyl chloride.....	C_4H_9Cl	2600360	2412746	173	13947
Chlorethylene.....	C_2H_3Cl	1193360	1130722	83	13617
Chloropropylene	C_3H_5Cl	1813480	1709250	125	13674
Allyl chloride.....	C_3H_5Cl	1818720	1714490	125	13716
Ethylene chloride....	$C_2H_4Cl_2$	1185440	1102056	80	13776
Ethylidene chloride ..	$C_2H_4Cl_2$	1185640	1102256	80	13778
Chloracetol	$C_6H_6Cl_2$	1815520	1690444	122	13840
Chloroform	$CHCl_3$	428120	407274	29	14044
Chlorethylene chloride	$C_2H_3Cl_3$	1049920	987382	71	13907
Tetrachlorethylene ...	C_2Cl_4	760280	760280	56	13576
Methyl bromide.....	CH_3Br	738840	676302	49	13802
Ethyl bromide.....	C_2H_5Br	1367280	1263050	91	13880
Propyl bromide	C_3H_7Br	1997160	1851238	133	13919
Allyl bromide.....	C_3H_5Br	1848480	1744250	127	13734
Methyl iodide.....	CH_3I	784320	721782	53	13619
Ethyl iodide.....	C_2H_5I	1414920	1310690	95	13797
				Average,	13796

Cyanogen Compounds.

Compound.	Formula.	4K. H_2O as liquid.	4K. H_2O as gas.	Divisor.	Quotient.
Hydrocyanic acid	HCN	634480	613634	45	13636
Cyanogen.....	C_2N_2	1038480	1038480	76	13664
Acetonitrile.....	C_2H_3N	1248560	1186022	87	13632
Propionitrile.....	C_3H_7N	1885800	1781570	129	13819
				Average,	13688

Amines.

Compound.	Formula.	4K. H_2O as liquid.	4K. H_2O as gas.	Divisor.	Quotient.
Methylamine	CH_5N	1033280	929050	69	13465
Ethylamine.....	C_2H_7N	1662680	1516758	111	13664
Propylamine.....	C_3H_9N	2302960	2115346	153	13826
Isobutylamine	$C_4H_{11}N$	2901440	2672134	195	13703
Amylamine.....	$C_5H_{13}N$	3562320	3291322	237	13423
Dimethylamine.....	C_2H_7N	1681840	1535918	111	13837
Diethylamine.....	$C_4H_{11}N$	2938000	2708694	195	13891
Trimethylamine	C_3H_9N	2330520	2142906	153	14006
Triethylamine	$C_6H_{15}N$	4209520	3896830	279	13967
Allylamine	C_3H_7N	2125120	1979198	147	13463
				Average,	13725

the factor is $3m$. In the amines it is $9m$. The divisors therefore become for cyanogen compounds, $12a + 6b + 3m - c - 8n$, and for amines, $12a + 6b + 9m - c - 8n$, the dividend in each case being $4K$ and the quotient a constant as heretofore. Leaving the oxygen compounds such as nitrates, etc., temporarily out of account, we have data for eighteen substances. Of these, ammonia, aniline, pyridine and piperidine are exceptional, and must be reserved for future consideration; the remaining fourteen are regular, as shown in the last tables.

In the combustion of organic sulphur compounds, at least in the cases given by Thomsen, SO_2 is produced, and this implies a distinct factor to be added to the divisor of the general formula. If s represents the number of molecules of SO_2 formed, the factor to be taken is $9s$, and the divisor becomes $12a + 6b + 9s - c - 8n$. Some of the compounds studied were cyanogen derivatives, and with these the factor $3m$ must also be taken into account, as in the nitriles, etc., which have already been considered. For thiophene, carbon disulphide, and carbonyl sulphide exceptional conditions hold, and their consideration will therefore be deferred. The remaining substances are as follows:

Compound.	Formula.	$4K$. H_2O as liquid.	$4K$. H_2O as gas.	Divisor.	Quotient.
Hydrogen sulphide ..	H_2S	546840	505148	38	13293
Methyl mercaptan....	CH_4S	1195240	1111856	80	13898
Ethyl mercaptan.....	C_2H_6S	1822600	1697524	122	13914
Methyl sulphide	C_2H_6S	1829400	1704324	122	13970
Ethyl sulphide.....	$C_4H_{10}S$	3068680	2964450	206	14390
Methyl sulphocyanide	C_2H_3NS	1595800	1533262	111	13813
Methyl mustard oil...	C_2H_3NS	1568240	1505702	111	13565
Allyl mustard oil.....	C_4H_5NS	2701440	2597210	189	13742
				Average,	13823

Two of the quotients in this group, it will be observed, are unsatisfactory, but as they diverge in opposite directions it is not necessary to reject them from the mean.

We have now examined the heats of combustion of seventy of the compounds studied by Thomsen. Fifty-five of these give close approximations to a constant when tested by the formula, and fifteen are either exceptional or erroneous. Many of the fifteen are explicable, but not without more detail than would be admis-

sible in a preliminary notice. My final memoir will deal with them all.

There still remain, unconsidered, about fifty other substances which contain, in addition to hydrogen and carbon, more or less oxygen within their molecules. They are therefore, upon burning, incompletely dissociated, for the oxygen atoms must remain combined with one or another of the elements associated with it. Furthermore, fewer external oxygen molecules are broken up during the process of combustion, and therefore the factor c of the general formula must undergo modification. The quantity n, also, no longer represents absolute dissociation of the molecule burned, and its significance, therefore, changes. The formula, however, with proper modifications, still applies, and the same constant appears as its quotient. For present purposes one series of compounds, the alcohols, will serve to illustrate the principle; the others must wait until some future time. In this series, still using quadrupled formulas for the sake of uniformity, the symbol c of the divisor represents the external oxygen consumed; and c_1 indicates the number of oxygen molecules contained in the alcohol. The formula then becomes

$$\frac{4K}{12a + 6b - c - c_1 - 8n} = \text{const.},$$

and the results of its application are as follows:

Compound.	Formula.	$4K$. H_2O as liquid.	$4K$. H_2O as gas.	Divisor.	Quotient.
Methyl alcohol.....	CH_4O	728920	645536	48	13448
Ethyl alcohol.....	C_2H_6O	1362120	1237044	90	13745
Propyl alcohol.....	C_3H_8O	1994520	1827752	132	13846
Isopropyl alcohol	C_3H_8O	1973280	1806512	132	13686
Isobutyl alcohol	$C_4H_{10}O$	2633960	2425550	174	13939
Trimethyl carbinol...	$C_4H_{10}O$	2565360	2356900	174	13546
Isoamyl alcohol.....	$C_5H_{12}O$	3280280	3030128	216	14028
Dimethylethyl carbinol.....	$C_5H_{12}O$	3241800	2891648	216	13387
Allyl alcohol	C_3H_6O	1859040	1733964	126	13762
Propargyl alcohol....	C_3H_4O	1724400	1641016	120	13675
Ethylene glycol.....	$C_2H_6O_2$	1192440	1067364	82	13017
				Average,	13646
				Omitting ethylene glycol,	13706

Taken altogether, the data so far presented summarize thus, the

figure given being, for each set of substances, the mean value of the quotient.

Hydrocarbons, 14 compounds.....	13873
Halogen compounds, 19 compounds.....	13796
Cyanides, 4 compounds	13688
Amines, 10 compounds.....	13725
Sulphur compounds, 8 compounds.....	13823
Alcohols, 11 compounds.....	13646
Average, 66 compounds	13773

What now, is the meaning of the formula used, and of the constant which is derived from it?

Before attempting to answer this question I may properly point out that the formula itself can be condensed and simplified. Taking the hydrocarbons, as the least complex of the series studied, the formula may be given in three forms, as follows:

$$\frac{4K}{12a + 6b - c - 8n} = \frac{4K}{11(a + \frac{b}{2}) - 8n} = \frac{4K}{11c - 8n} = \text{const.}$$

The difference between these expressions arises from the fact that the oxygen used is always proportional to the carbon and hydrogen burned, but all three give the same quotient. The first and most elaborate form, however, is the one to be preferred, for the reason that it gives in detail all the factors of the original equations. In it the constant appears as a function of all the changes which have taken place, the substances produced being indicated with the plus sign, while the substances destroyed are represented by minus quantities. The other formulas may be easier to apply, but they are much less simple to interpret.

Looking now to the constant itself, 13,773, we see that it is sensibly identical in value, within the limits of experimental uncertainty, with the neutralization constant of 13,700 calories. The latter is purely chemical in its character, uncomplicated by extraneous physical considerations, and it represents a union of the simplest kind, one bond joining two ions. In short, it seems to be a definite unit of thermochemical change, of which the quantities discussed in this paper are multiples, and by whose aid the original equations, hitherto indeterminate, may be satisfied. Let us examine the general formula in more detail.

If we take the constant 13,773 calories as our unit, the fundamental formula may be written

$$\frac{4K}{12a + 6b - c - 8n} = 1, \text{ or one unit,}$$

and hence, $12a + 6b - c - 8n = 4K$; that is, each molecule of a or CO_2 produced by the combustion has a value of 12 units, each molecule of water is represented by 6 units, each molecule of oxygen by 1, and each atomic linking in one molecule of the substance under investigation by 8/4, or 2. These quantities represent the actual heat of formation of the several molecules from gaseous, dissociated atoms, and when they are introduced into the original equations the latter are satisfied.

Let us recur to the equation for methane:

$$x + 2y - 2z - r = 191{,}084.$$

$$\begin{aligned} x &= 12 \times \quad 13773 = \quad 165276 \\ 2y &= 12 \times \quad 13773 = \quad 165276 \\ -2z &= \quad 2 \times (-13773) = - \quad 27566 \\ -r &= \quad 8 \times (-13773) = - 110184 \\ &\qquad\qquad \text{Sum} = 192822 \end{aligned}$$

a quantity which exceeds Thomsen's mean value by 0.91 per cent. As Thomsen's separate determinations vary among themselves by 0.99 per cent., the agreement is satisfactory. The calculated value is about 0.2 per cent. higher than his highest.

This one example is enough to show, for present purposes, the method of computation, but to illustrate its effectiveness a few more instances may be given in condensed form. Each equation represents the combustion of four molecules of the substance named, the water produced being reckoned as gaseous.

Compound.	Equation	Calculated.	Variation. Per cent.
Ethane.....	$8x + 12y - 14z - 4r = 1356684$	1349754	0.51
Propylene.....	$12x + 12y - 18z - 4r = 1845884$	1845582	0.04
Methyl chloride	$4x + 6y + 2h - 7z - 4r = 645262$	647331	0.32
Allyl bromide..	$12x + 10y + 2h_1 - 17z - 4r = 1744250$	1749171	0.28
Ethyl iodide...	$8x + 10y + 2h_2 - 13z - 4r = 1310690$	1308435	0.17
Propionitrile ..	$12x + 14y + 2m - 19z - 4r = 1781570$	1776717	0.28
Ethylamine ...	$8x + 14y + 2m - 15z - 4r = 1516758$	1528803	0.79

The agreements, as shown in the percentage column, are reasonably close; the absolute variations, to be compared with Thomsen's data, should be divided by four. It must be remembered that Thomsen's determinations vary among themselves; that they

represent measurements at constant pressure and not at constant volume; that there is a small uncertainty in the adjustment from liquid to gaseous water; and that other unnoted corrections should possibly be applied. Take it for all in all, the validity of the constant may be looked upon as established, and a fair estimate of absolute thermochemical values has been attained. The neutralization constant, as determined with different acids and bases, shows fully as great variations, and yet there can be little doubt as to its authenticity and meaning.

It would be most unwise to assume, from the evidence here presented, that the constant under discussion governs all chemical combinations. It applies to the classes of compounds considered in this paper, but there are others to which, in all reasonable probability, it does not apply. Its significance, however, is very great, and it suggests a general law. *In any class of compounds, the heat of formation is proportional to the number of atomic linkings within the molecule, and seems to bear no relation to the masses of the atoms which are combined.* Among organic substances, this relation is very clear, and is implied in the factor $8n$ which occurs in all forms of the general formula. For these compounds the fundamental unit appears to be double the constant, or 27,600 in round numbers. Multiply this by four, the number of unions in the molecule, and we have the *absolute* heats of formation, from gaseous, dissociated atoms, of methane, of methyl chloride, bromide, or iodide, and of chloroform, all these quantities being equal. Multiply by seven, and the value for ethane is obtained, and so on throughout the aliphatic hydrocarbons and their immediate derivatives. For other compounds, as in the aromatic group, the coefficent of n seems to be other than 8, but here the actual number of atomic unions is uncertain. For inorganic substances, considered in the gaseous state, the data are too few, and constants of different magnitude may control their formation. On this subject, speculation would be premature, and I must reserve my conclusions regarding it until later. Probably, however, the general principle will hold, and the absolute heat of formation of any substance will prove to be a function of the number of atomic unions within the molecule; that is, of the number of chemical acts involved in its production.

A NEW GLASS OF LOW SOLUBILITY.[1]

By G. E. Barton

Received June 7, 1902.

The statement in a recent number of *Science*[2] to the effect that American glass is inferior to that made in Germany is without doubt true if for "Germany" we read "Jena". The grounds for the claim that at least one glass made in this country heretofore has been equal to anything made on the continent except Jena glass, I submit herewith. I have here, also, samples of a glass of my own devising which I believe is the equal of the Jena glass as regards its resistance to water, acids and carbonates, and superior in its resistance to caustic alkali solutions. Before presenting the figures, however, a brief résumé of the method by which they were obtained and the reason for its choice in preference to others is submitted.

In deciding upon this method for testing the comparative solubility of different glasses, I have passed over the beautiful work of Pfeiffer, Kohlrausch, Mylius and Foerster, all of whom have compared different glasses by determining the amount of bases which go into solution upon treating them with water, either by conductivity or purely chemical methods, for a method which is not particularly novel, but gives results in the ordinary units of the chemist.

The method employed was as follows: pint, globe, flat-bottomed flasks were rinsed in chemically pure ammonium hydroxide, then in water, then in chemically pure hydrochloric acid, then in water, and finally with alcohol and ether, after which they were dried at the temperature of the room by a current of dry air, carefully wiped with a towel, and allowed to stand exactly one-half hour before weighing. The weighing was carried to 0.1 mg. with the ordinary precautions of analytical chemistry. I am aware that the glass could not have been free from water at the time of weighing, but every effort was made to insure as uniform a state as regards moisture as possible.

The flasks after weighing were partially filled with exactly 300

[1] Read at the Pittsburg meeting of the American Chemical Society, July 2, 1902.

[2] "It is claimed that American glass is inferior to German in quality and power of resistance to chemicals." Excerpts from the Report of the Census Committee of the American Chemical Society, *Science*, 15, 813.

cc. of a 1 per cent. solution of sodium carbonate, attached to an inverted condenser by a rubber stopper, and boiled for exactly three hours over an asbestos plate one-sixteenth inch thick heated by a Bunsen burner, the latter being so regulated as to produce as slow but constant an ebullition as possible. The level of the liquid was not appreciably lowered in the three hours. At the end of this time the flasks were disconnected, emptied, rinsed with water three times, then treated precisely as before the boiling, and weighed. 300 cc. of water were next used, then 300 cc. of a solution containing 0.4 per cent. of hydrochloric acid, and finally the same quantity of a 1 per cent. solution of sodium hydroxide, the weighing, rinsing and drying always being carried out as above described.

That this method gives results sufficiently accurate for factory control I have proved repeatedly. It has the great advantage that it can be applied by any one in almost any laboratory, as it only requires the ordinary forms of apparatus and reagents, and if used for comparing two samples of glass, no particular care as to the exact strength of the solutions used is necessary, provided only both are treated alike. The greatest cause of variation in testing the ordinary quality of chemical ware is that the surface layer of the glass, after partial extraction with the solvent, is more or less completely removed by the mechanical action of the escaping steam. This cause of variation becomes almost nothing, however, in testing glasses like the Jena normal glass and the new glass.

Mylius and Foerster[1] found that the ratio of the bases to silicic acid in the aqueous solution obtained by boiling water five hours in flasks, varied from 1:0.21 to 1:1.6, the figures being for a poor glass from Thuringia and Kavalier's glass respectively. From this it is plain that no conclusions as to the total amounts going into solution can be drawn with safety from the results of any method which only gives the amount of bases taken up. It is also clear that such a method cannot be used for comparing glasses so totally different in composition as those made by Schott at Jena and by Kavalier in Bohemia. While the unavoidable variations (when testing by the method I used) between different results with the same glass are sometimes rather large, it is also certain that they are equally great in using the ware, so that an average of

[1] *Zischr. anal. Chem.*, 31, 245.

a sufficient number of results comes nearer representing actual practice than anything else that has been proposed.

Each of the following figures is an average of three results and represents the loss in milligrams sustained by flasks when tested as described:

LOSS PER FLASK EXPRESSED IN MILLIGRAMS.

	Whitall-Tatum Co.	Kavalier.	Jena.	New glass.
One per cent. sodium carbonate solution	134.4	126.6	30.6	32.3
Water	8.4	20.6	1.1	0.7
Two-fifths per cent. hydrochloric acid solution	4.7	16.2	1.3	1.5
One per cent. sodium hydroxide solution	100.1	78.4	97.1	89.0
Total loss	247.6	241.8	130.1	123.5

The variations between the new glass and the Jena glass are, with the exception of the solubility in 1 per cent. sodium hydroxide solution, within the limits of factory practice. In resisting caustic soda solution, however, the new glass is undoubtedly superior to the Jena glass.

It may not be out of place at this time to call attention to the fact that beakers made of either the new glass or Jena glass can be used for evaporations on the water-bath without danger of cracking. A few tests of beakers made from other kinds of glass will convince one that very few pieces will stand exposure to steam for more than fifty hours. I have exposed beakers of both the new and Jena glass to the action of steam for over 200 hours continuously, without any sign of fracture appearing.

CHEMICAL LABORATORY OF WHITALL TATUM COMPANY,
June 4, 1902.

NOTES.

Rapid Volumetric Method for Determining Phosphoric Acid in Fertilizers.—In describing the following volumetric method for the determination of phosphoric acid in fertilizers and fertilizing materials very little that is strictly original is claimed. The method is a modification of the volumetric method as published by the Association of Official Agricultural Chemists. The most important change consists in shaking the solution after adding the ammonium molybdate.

Under ordinary conditions the method can be completed in about thirty minutes from the time the sample is received at the laboratory. A great many determinations have been made in twenty minutes which agreed in duplicate to the second decimal place and which did not vary over 0.1 per cent. from a careful gravimetric determination. Over 3000 determinations have been made by the method during the regular work of the laboratory on samples ranging from 1 per cent. up to 47 per cent. phosphoric acid. Between these very wide limits it seems to be all that could be desired both for rapidity and accuracy.

The following table will illustrate the very close agreement of duplicate determinations with each other and with the gravimetric method of the Official Agricultural Chemists.

Two grams of the sample were digested and made up to 250 cc.

	Time taken in making determination.	Aliquot part in grams.	Per cent. of phosphorus pentoxide by volumetric method.	by gravimetric method.
1. 10 cc. used	20 minutes	0.08	15.05	
2. 15 cc. used	30 minutes	0.12	15.00	
3. 20 cc. used		0.16		15.04
4. 25 cc. used	1 hour	0.20	15.00	
5. 30 cc. used	Yellow precipitate stood over night	0.24	14.94	

Method: Weigh 2 grams of the prepared sample into a 200 cc. beaker, add about 10 cc. strong hydrochloric acid, mix by shaking, wash down the sides of the beaker with about 10 cc. of water, cover the beaker with a watch-glass, and boil briskly. With the watch-glass slightly raised, add slowly from 1 to 2 grams of sodium chlorate or enough to decompose the organic matter excepting fat. Boil off the excess of free chlorine. Dilute with water and transfer the contents of the beaker to a 250 cc. measuring flask. Cool and make up to the mark. In case no fat is present, filtration is usually unnecessary as a small amount of insoluble residue will not influence the titration. Transfer an aliquot part of 25 cc., representing 0.2 gram of the original sample, to a 200 cc. Erlenmeyer flask, add 15 cc. ammonia (sp. gr. 0.90) and a small piece of litmus paper. Neutralize the ammonia with strong nitric acid, using a slight excess only. The temperature of the solution is now about 65° C. If more than 2° or 3° above this temperature add cold water to bring it down to 65° C. Now add from 25 cc. to 75 cc. ammonium molybdate solution, depending on the amount

of phosphorus pentoxide in the sample, and shake vigorously by hand. Mechanical shaking is of but slight advantage. The precipitate will settle out clear very quickly. Filter with suction through a 9 cm. filter-paper. Wash the precipitate free from acid with water, making no effort to remove the precipitate from the flask. The washing will take about two minutes. Test the filtrate by adding more ammonium molybdate solution and heating to 65° C. Transfer the precipitate and filter-paper to the Erlenmeyer flask, and run in standard alkali until the yellow precipitate is nearly dissolved. Shake to disintegrate the filter-paper. Now add 1 cc. phenolphthalein solution as indicator and continue adding the alkali cautiously until the pink color remains permanent for about a minute. The end-reaction is very sharp. In case an excess of alkali is added it can be titrated back with standard acid. Divide the burette reading by two and the result will be the per cent. of P_2O_5 in the sample.

Preparation of Reagents.

(*a*) Molybdic Solution: This solution is made as directed in Bulletin No. 46, Revised Edition, U. S. Department of Agriculture, Division of Chemistry, except that the solution is heated for five hours in a bath of water at a temperature of 65° to 67° C.

(*b*) Standard Potassium Hydroxide Solution: This is prepared by diluting 323.81 cc. of normal potassium hydroxide, free from carbonates, to 1 liter. One cc. is equal to 1 mg. phosphorus pentoxide.

(*c*) Standard Sulphuric Acid Solution: The strength of this solution is the same as that of the standard alkali.

(*d*) Phenolphthalein Solution: One gram of phenolphthalein is dissolved in 100 cc. of 50 per cent. alcohol. A. L. EMERY.

New Apparatus in Water Analysis.—In the June number of this Journal (p. 537) Messrs. Thomas and Hall describe under the above heading an apparatus for collecting samples of water for the determination of dissolved oxygen or carbon dioxide. While the apparatus may be a convenient one for this purpose, it seems a just criticism to point out that samples collected in this way will not represent the exact character of the water being tested and that, too, where results of the greatest accuracy possible are required. Suppose the sample is to be collected from the bottom of

a deep pond where the oxygen at most amounts to only a few tenths per cent. of saturation. The entering water will come in contact with the air in the bottle and will undoubtedly absorb some oxygen. It has been found in our work that when the dissolved oxygen content of the water is very low it is always necessary to aspirate through the calibrated bottle *at least several times its volume* of the water in order to be sure that the first portions entering the bottle shall be completely displaced. In the apparatus described no provision is made for this and it will be evident that in such cases the results will not be accurate. The same criticism will apply, though perhaps not with the same force, to determinations of carbon dioxide made on samples collected in this way.

A. G. WOODMAN.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS, June 10, 1902.

NEW BOOKS.

GRUNDRISS DER QUALITATIVEN ANALYSE VOM STANDPUNKTE DER LEHRE VON DEN IONEN. BY DR. WILH. BÖTTGER. Leipsic. 1902. 250 pp. + 15 pp. of tables.

This book may be briefly characterized as an interpretation in detail of the usual scheme of qualitative analysis with the help of the Laws of Chemical Equilibrium and the Ionic Theory. It differs from Ostwald's "Scientific Foundations of Analytical Chemistry" in the respect that the theoretical principles involved are gradually introduced in connection with the analytical procedure, instead of as an introduction to it; and in the respect that it is intended to serve as a working manual for a course of qualitative analysis, rather than as an accompaniment to such a course. It differs from the recent treatise of Treadwell on the same subject in that it is far less extensive and complete on the experimental side, and in that the theoretical interpretation of the reactions is given greater prominence. In fact, the point of view from which the book is written would seem to make it fitted to teach laws and theoretical principles with the help of qualitative analysis, rather than qualitative analysis with the help of the principles. And, correspondingly, for the training of exact analysts, the book can not be said to be fully satisfactory; for the conditions for securing

certainty and delicacy in the tests are often not sufficiently indicated. Moreover, the directions for laboratory experiments are either so incomplete or so interwoven with descriptions and theoretical explanations, that some difficulty would be met with in the use of the book as a laboratory manual. In spite, however, of these and other defects in the manner of presentation, the book is a very valuable contribution to the science, and well deserves the attention of students, and especially of teachers, of the subject; for it represents the first systematic attempt at a detailed interpretation of the reactions of qualitative analysis from the standpoint of modern theoretical chemistry, carried out by an author who shows himself to be thoroughly familiar with the principles involved.

To illustrate more fully the character of the book, the following summarized statement of its contents may be presented. After a very brief introduction, the author describes the precipitation and separation of lead, silver, and mercurous mercury; discusses incidentally filtration, washing, the significance of solubility and equilibrium in general; and presents the fundamental hypothesis of the Ionic Theory,—unfortunately in a somewhat intangible form, since, following the practice of Ostwald, the author avoids using the concepts of the Atomic Theory. He then describes and interprets the important additional reactions of these metals, introducing the subject of complex ions and their effects in increasing solubility in connection with the silver-ammonia and silver-cyanogen compounds. The precipitation and separation of the metals of the hydrogen sulphide group are next described, theoretical explanations being interwoven with the procedure at each step. Incidentally, the Mass-Action Law in its general form is brought in, and is applied to the hydrogen sulphide precipitation. Additional reactions of the metals of the group are then discussed, and the varying degree of dissociation of different substances is referred to.

In connecton with the succeeding groups of metals a similar plan is followed. The principles relating to oxidation and reduction, to the precipitation by ammonia of alkaline-earth phosphates, to hydrolysis, and to colloids, are treated under the aluminum and iron groups. Unfortunately, the solubility-product principle and the equilibrium-equation for dissolved electrolytes are not taken up till the calcium group is reached. By reason of

this fact the explanations of many points in the scheme of analysis for metals are so incomplete that much of the gain which should result from the application of the Ionic Theory is not realized.

The second part of the book is devoted to the detection and reactions of the acid radicals or anions. This part, consisting of sixty pages, is unusually thorough and complete. The dissociation-relations of the various acids, the subjects of catalysis and of fractional solution and crystallization, the principle of valence, and other theoretical considerations are introduced.

The third part of the book treats at length of the preliminary examination in the dry way, and of the methods of preparation of solutions for analysis. A number of special procedures adapted to the different insoluble substances are described.

A fourth part consisting of thirty-three pages, is devoted to the reactions of the rarer metals,—a subject too often neglected.

A set of tables, in the form of a separate pamphlet, summarizing the whole procedure, and intended for laboratory use, accompanies the book.

An English translation is in preparation, which will make this valuable work available for the use of elementary students.

ARTHUR A. NOYES.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 64.]

A NEW SEPARATION OF THORIUM FROM CERIUM, LANTHANUM, AND DIDYMIUM, AND ITS APPLICATION TO THE ANALYSIS OF MONAZITE.[1]

BY FLOYD J. METZGER.

Received June 10, 1902.

THE marked disagreement, among well-recognized chemists, in the determination of thorium in monazite sand, seemed sufficient to warrant a more careful investigation of the methods now existing for its determination, and it was with this object in view that the following work was undertaken.

By thorium, is meant the element as it was generally understood before the more recent researches of Brauner and Baskerville, which point quite conclusively toward the isolation of a new element from what is now generally called thorium.

REVIEW OF METHODS.

Among the methods proposed for the separation and purification of thorium, the following may be mentioned as the most important.

Bahr[2] was the first to notice that thorium oxalate was soluble in a hot concentrated solution of ammonium oxalate. Since that

[1] Read at the meeting of the New York Section of the American Chemical Society, June 6, 1902.

[2] *Ann. Chem.* (Liebig), 132, 231 (1864).

time numerous investigators, namely, R. Bunsen,[1] C. Glaser,[2] Hintz and Weber[3] and others, have attempted to perfect the separation and have found that a complete separation of thorium from the other rare earths, in the form of oxalates, cannot be made by one extraction with a hot concentrated solution of ammonium oxalate, but that the operation has to be repeated several times.

The separation of thorium from the other rare earths by using sodium thiosulphate was first proposed by Chydenius[4] and later worked by Hermann,[5] Drossbach,[6] Hintz and Weber,[7] and others.

The separation is based on the fact that thorium is precipitated from a neutral or slightly acid solution, by sodium thiosulphate, while cerium and the other rare earths remain in solution.

As was pointed out by Chydenius[8] and also Glaser,[9] the precipitation is not complete in one operation, but by reprecipitating the filtrate with ammonia, converting this into the chloride and reprecipitating with sodium thiosulphate (repeating as long as a precipitate is obtained with sodium thiosulphate), a complete separation is obtained.

Hintz and Weber[10] say the separation works best in dilute solutions and in the presence of two or three drops of dilute hydrochloric acid and give this method preference.

Cleve[11] was the first to show that thorium could be precipitated by hydrogen peroxide from a sulphate solution, and that the precipitate had the composition represented by the formula $Th_4O_7SO_3$.

Boisbaudran[12] also used hydrogen peroxide as a precipitant about the same time.

Wyrouboff and Verneuil[13] carried the investigation a little farther and showed that an analogous precipitate of thorium could be obtained from a solution of the nitrate (*i. e.*, $Th_4O_7N_2O_5$) and

[1] Pogg. *Ann.*, **155**, 380 (1875).
[2] *Ztschr. anal. Chem.*, **36**, 213 (1897).
[3] *Ibid.*, **36**, 27 (1897).
[4] Pogg. *Ann.*, **119**, 46.
[5] *J. prakt. Chem*, **93**, 106.
[6] *Ztschr. angew. Chem.*, (1901), p. 655.
[7] *Ztschr. anal. Chem.*, **36**, 676 (1897); *Ibid.*, **35**, 525.
[8] *Loc. cit.*
[9] *Chem. Ztg.*, **20**, 612 (1896).
[10] *Loc. cit.*
[11] *Bull. Soc. Chim.*, **43**, 53 (1885).
[12] *Compt. rend.*, **100**, 605.
[13] *Ibid.*, **126**, 340 (1898).

that it gave a complete separation of thorium from the other rare earths.

Kosmann[1] separated the greater part of the didymium salt from the crude material, as sulphate. Then he separated thorium from cerium, lanthanum and didymium by successive treatment of the acid solution with hydrogen peroxide solution, an acid-ammonium citrate solution, and ammonia. A precipitate of aluminum phosphate and thorium hydroxide was formed which was afterwards separated by oxalic acid.

Various other methods which are well worth mentioning are: Urbain[2] used acetylacetonate of sodium. Chavastelon[3] separated thorium by means of sodium sulphite. Boisbaudran[4] precipitated thorium, after reducing the cerium, with cuprous oxide. Dennis[5] used potassium nitride. Delafontaine[6] separated thorium from zirconium by fusion with potassium acid fluoride and leaching out the double potassium-zirconium fluoride with hot water. Muthmann and Baur[7] employed potassium chromate. Kersten[8] based a method upon the difference in solubility of the oxides in hydrochloric acid. Nilson[9] precipitated the hydrated sulphate of thorium.

Undoubtedly the best method which has yet been published for the complete analysis of monazite is that of Glaser.[10]

Benz,[11] in a recent article, makes a very careful study of the methods now employed for the analysis of monazite (the ammonium oxalate, thiosulphate and hydrogen peroxide methods) and gives a good comparison of their accuracy.

He finds that one digestion of the mixed oxalates with even a large excess of ammonium oxalate is insufficient to bring into solution all the thorium; on the contrary he finds that only about one-half the thorium is dissolved, and that after repeated digestions considerable cerium is brought into solution.

[1] *Chem. Centrbl.*, (1897), Part 1, 837.
[2] *Bull. Soc. Chim.*, **18**, 347 (1896).
[3] *Chem. Centrlbl.*, 1, 876 (1900).
[4] *Chem. News*, **50**, 201 (1884); also *Compt. rend.*, **99**, 525 (1884).
[5] *Am. Chem. J.*, **16**, 79 (1894); also This Journal, **18**, 947 (1896).
[6] *Chem. News*, **75**, 230 (1897).
[7] *Ber. d. chem. Ges.*, **332**, 2028 (1900).
[8] Pogg. *Ann.*, **47**, 385 (1839).
[9] *Ber. d. chem. Ges.*, (1882), p. 2521; *Ibid.*, (1887), p. 1666.
[10] This Journal, **18**, 789 (1896).
[11] *Zischr. angew. Chem.* (1902), p. 297.

With the thiosulphate method he gets very good results after three or four precipitations, and obtains the thoria almost without a trace of cerium. This, however, has the disadvantage of being extremely long.

Hydrogen peroxide, as he shows, precipitates thorium completely from a neutral solution, or from a solution very faintly acid with nitric acid. It also separates thorium from cerium and lanthanum by one reprecipitation.

EXPERIMENTAL.

VARIOUS PRECIPITANTS TRIED.

As very few weak organic acids have hitherto been employed for the separation of thorium from its associated rare earths, the following were tried:

Maleic Acid.—Aqueous solutions of maleic acid with thorium cerium, lanthanum and didymium give no precipitate hot or cold. Solutions of cerium, lanthanum and didymium in 50 per cent. alcohol, give nothing hot or cold. A solution of thorium in 50 per cent. alcohol, gives no precipitate in the cold, but on heating, a partial precipitation results.

Cinnamic Acid produces at least a partial precipitation of thorium from 20 per cent. alcoholic solutions. The precipitate cannot be filtered (runs through) and for this reason the completeness of the precipitation was not determined. Cerium, lanthanum and didymium give nothing under the same conditions.

Picric Acid and thorium, in alcoholic solutions, give a partial precipitation of thorium. Cerium, lanthanum and didymium give no precipitate under these conditions.

Phthalic Acid in aqueous solution with cerium, lanthanum and didymium gives nothing cold or hot. Thorium, however, in aqueous solution with phthalic acid gives a partial precipitation on heating. From alcoholic solutions a heavy curdy precipitate results on heating, and is approximately half complete. Cerium, lanthanum and didymium in alcoholic solutions with phthalic acid give no precipitate.

Fumaric Acid.—Aqueous solutions, hot or cold, give nothing with cerium, lanthanum or didymium. Thorium and fumaric acid in aqueous solutions give a precipitate in the cold, which forms slowly, but on applying heat the precipitate forms rapidly

(white, flocculent), settles out nicely, and is almost complete. From solution in 95 per cent. alcohol, fumaric acid precipitates thorium quantitatively even in the cold. Cerium and fumaric acid in 95 per cent. alcohol give no precipitate in the cold, but, on heating, a small fraction of the cerium is thrown down. Lanthanum and didymium in 95 per cent. alcohol give nothing cold or hot. From solutions in 40 per cent. alcohol, fumaric acid gives a quantitative precipitation of thorium on heating; lanthanum and didymium under the same conditions give nothing. Cerium in 40 per cent. alcohol gives, with fumaric acid, nothing cold or hot, unless the cerium solution is quite strong, when a very small fraction is precipitated.

Ammonium Fumarate precipitates thorium, cerium, lanthanum and didymium from aqueous solutions, insoluble in excess, soluble in mineral acids.

Among the amido and amino compounds tried were:

Urea gave nothing.

Thiourea gave nothing.

Acetamide gave nothing.

Semicarbazine gave nothing.

Succinimide gives no precipitation of cerium, but gives a partial precipitation or thorium from alcoholic solutions.

Diethylamine precipitates thorium, cerium, lanthanum and didymium.

THE QUANTITATIVE PRECIPITATION OF THORIUM BY FUMARIC ACID.

From the experiments given on a preceding page it was now evident that thorium could be precipitated quantitatively from alcoholic solutions, leaving cerium, lanthanum and didymium in solution. It was desirable to know the smallest quantity of alcohol necessary to effect this precipitation, and still leave the cerium, lanthanum and didymium in solution. This strength was reached when the solution contained 40 per cent. of alcohol.

The following results will show the completeness of the precipitation from the various strengths of solution:

Alcohol. Per cent.	Volume. cc.	ThO_2. Taken.	Found.
15	150	0.1568	0.1508
35	150	0.1568	0.1551
40	200	0.1961	0.1962
40	150	0.1568	0.1561
40	120	0.1176	0.1176
40	120	0.2007	0.2003
40	100	0.1004	0.1006
40	120	0.1176	0.1179
40	200	0.1961	0.1962

SEPARATION OF THORIUM FROM CERIUM, LANTHANUM AND DIDYMIUM.

The salts used for the experiments were the best nitrates that could be purchased, and the thorium nitrate was purified according to the method suggested by Wyrouboff and Verneuil[1] which is as follows:

Eighty-three grams of the nitrate, corresponding approximately to 39 grams of thoria, were dissolved in 8 liters of water. The solution was divided equally in twelve beakers and precipitated with hydrogen peroxide (10 cc. hydrogen dioxide for every 0.5 gram thorium dioxide). The solutions were then heated to 85° C. and allowed to settle. The precipitates were washed a dozen times by decantation with hot water, and then transferred to a large Büchner funnel, and the washing continued until the filtrate gave no precipitate with ammonia. The precipitate was then transferred to a large porcelain evaporating dish and 150 cc. of concentrated nitric acid added; heat was applied and the whole went into solution readily. The solution was evaporated to dryness, taken up in water, diluted to 8 liters, and the process repeated. The filtrate from the hydrogen peroxide precipitation was treated with ammonia and hydrogen peroxide, giving a brown precipitate of cerium trioxide. This precipitate of cerium peroxide was examined for lanthanum and didymium, but none could be detected.

A stock solution was made of this purified thorium nitrate and standardized very carefully by precipitation with oxalic acid. This was the thorium used for the experiments. A cold saturated solution of fumaric acid in 40 per cent. alcohol (containing approximately 0.1 gram per 10 cc.) was used as the precipitant.

[1] *Compt. rend.*, **126**, 4, 340 (1898).

METHOD OF ANALYSIS.

Make the solution of the neutral nitrate 40 per cent. alcohol (volume about 150-175 cc. with 0.1 to 0.2 gram thorium dioxide and about the same amount of admixed oxides), then add 12 to 15 cc. of fumaric acid solution (about 0.10 gram per 10 cc.) for each 0.1 gram thorium dioxide and heat to boiling (75° to 80° C.); allow to stand a few minutes until the precipitate settles, then filter (while still hot) through a long stem funnel, or by suction. Wash the precipitate four or five times with hot 40 per cent. alcohol, then put paper and precipitate into a platinum crucible, ignite, and weigh as thorium dioxide. A number of analyses were made in this way using mixtures of thorium with cerium, lanthanum and didymium and it was found that the thorium invariably carried with it an appreciable quantity of the impurity which could not be washed out, nor could it be prevented by the addition of such salts as ammonium chloride, ammonium nitrate, etc.

A few results will show the extent to which these impurities are carried down.

CeO_2.	La_2O_3.	Di_2O_3.	Fumaric acid. cc.	Volume. cc.	ThO_2. Taken.	ThO_2. Found.
0.2000			25	150	0.1725	0.1730
0.2000			25	150	0.1961	0.1982
.....	0.2000		25	150	0.1921	0.1941
.....	0.2000		25	150	0.1961	0.1990
.....	0.2000		25	150	0.1882	0.1907
.....	0.2000		25	150	0.1961	0.1978
.....		0.2000	25	150	0.1961	0.1992
.....		0.2000	25	150	0.1961	0.1972
.....		0.2000	25	150	0.1882	0.1901
.....		0.2000	25	150	0.1961	0.1979

Reprecipitation was next tried, and gave very satisfactory results. For this reprecipitation it is only necessary to dissolve the precipitate of thorium fumarate (formed by the first precipitation) off the filter in hot dilute hydrochloric acid—or better, place the paper and precipitate back into the beaker, add a little dilute hydrochloric acid, heat, then filter off the paper—and evaporate to dryness on a water-bath. During the process of this evaporation some of the salt adheres to the sides of the beaker, but this is easily obviated by shaking the beaker occasionally and washing down with a few drops of water from a wash-bottle.

When the residue is free from acid (better add a few cubic centimeters of water and evaporate a second time), add about 50 cc. water (leaving the beaker on the water-bath) and stir the residue loose from the bottom with a rubber-capped stirring rod; some carbonaceous matter from the fumaric acid, partly decomposed, and also some fumaric acid and a trace of thorium fumarate will remain insoluble at this point, but need not be regarded. Add alcohol sufficient to make the solution 40 per cent., dilute to the proper volume wth 40 per cent. alcohol, add a little fumaric acid (8 to 10 cc.) and precipitate as before; wash, ignite and weigh.

Hydrochloric acid was used instead of nitric for the solution of the thorium fumarate, for the reason that nitric acid formed, on evaporation, a deposit which was practically insoluble in water.

The following results will show the accuracy of the separation:

			Fumaric acid.	Volume.	ThO_2.	
CeO_2.	La_2O_3.	Di_2O_3.	cc.	cc.	Taken.	Found.
0.2000			25	150	0.1961	0.1966
0.2000			25	150	0.1961	0.1957
.....	0.2000		25	150	0.1961	0.1964
.....	0.2000		25	150	0.1961	0.1959
.....		0.2000	25	150	0.1961	0.1965
.....		0.2000	25	150	0.1968	0.1965

Mixtures of thorium, cerium, lanthanum and didymium were then made in the proportions in which they are usually found in monazite sand, and analyzed the same as above with these results:

			Fumaric acid.	Volume.	ThO_2.	
CeO_2.	La_2O_3.	Di_2O_3.	cc.	cc.	Taken.	Found.
0.283	0.133	0.157	10	175	0.0557	0.0558
0.283	0.133	0.157	25	200	0.0572	0.0571
0.283	0.133	0.157	10	175	0.0572	0.0574
0.283	0.133	0.157	10	175	0.0557	0.0558
0.566	0.266	0.314	15	350	0.1115	0.1114
0.566	0.266	0.314	15	350	0.1129	0.1132

Mixtures containing equal amounts of thorium, cerium, lanthanum and didymium, and mixtures containing thorium in excess were then analyzed as follows:

			Fumaric acid.	Volume.	ThO_2.	
CeO_2.	Ta_2O_5.	Di_2N_2.	cc.	cc.	Taken.	Found.
0.1000	0.1000	0.1000	10	120	0.0995	0.0990
0.1000	0.1000	0.1000	10	120	0.1003	0.0995
0.1000	0.1000	0.1000	25	130	0.1529	0.1523

CeO_2.	La_2O_3.	Di_2O_3.	Fumaric acid. cc.	Volume. cc.	ThO_2. Taken.	ThO_2. Found.
0.1000	0.1000	0.1000	40	150	0.2007	0.2002
0.1000	0.1000	0.1000	40	150	0.2015	0.2010
0.1000	0.1000	0.1000	60	150	0.3011	0.3005
0.1000	0.1000	0.1000	60	150	0.3019	0.3023
0.0500	0.0500	0.0500	25	200	0.1961	0.1963
0.0500	0.0500	0.0500	25	200	0.1968	0.1969
0.0250	0.0250	0.0250	25	200	0.1976	0.1971
0.0250	0.0250	0.0250	25	200	0.1991	0.1985

EFFECT OF SALTS WITH ACETIC RADICALS ON THE PRECIPITATION OF THORIUM BY FUMARIC ACID.

A very peculiar effect is noticed when an acetate is added to a solution of the rare earths (cerium, lanthanum, didymium, etc.), which has already had added to it some fumaric acid. The results are these:

Take a solution of cerium (lanthanum or didymium) in 40 per cent. alcohol and add to it a solution of fumaric acid; nothing results. If now, one or two drops of ammonium acetate is added to this mixture of cerium and fumaric acid, the cerium is precipitated completely. Then if to this solution containing the precipitate an excess of ammonium acetate is added, the whole redissolves and leaves a clear solution. Cerium (lanthanum or didymium) is not precipitated by ammonium acetate alone. Ammonium fumarate precipitates cerium (lanthanum or didymium) insoluble in excess of precipitant. Add to cerium (lanthanum or didymium) dissolved in 40 per cent. alcohol, fumaric acid, and then one or two drops of acetic acid, and nothing results; but then by adding to this one or two drops of ammonium acetate, the cerium is thrown down quantitatively as before. Thorium differs from cerium, lanthanum and didymium in that the precipitate formed by fumaric acid is only partially soluble in an excess of ammonium acetate. Sodium acetate has the same effect as ammonium acetate.

The exact reaction in the above experiments has not yet been studied, but it is quite evident that salts of acetic acid must be avoided in the separation of thorium from cerium, lanthanum and didymium by fumaric acid.

THE EFFECT OF OTHER METALS ON THE SEPARATION.

It was very desirable to know the effect of other metals on the

precipitation of thorium by fumaric acid, so all the metals available were tried. The solutions in all cases (where such solutions could be obtained) were made in 40 per cent. alcohol and the fumaric acid added. The following salts were tried:

$CuSO_4$; $AgNO_3$; $AuCl_3$ (acid); $MgCl_2$; $CaCl_2$; $Sr(NO_3)_2$; $BaCl_2$; $ZnSO_4$; $CdCl_2$; $Hg_2(NO_3)_2$; $Hg(NO_3)_2$; $HgCl_2$; H_3BO_3; $Na_2B_4O_7$; Al_2Cl_6; $SnCl_4$ (acid); $SnCl_2$ (acid); $Pb(NO_3)_2$; $MnCl_2$; Na_2HPO_4; As_2O_3 (slightly sol.); Sb (tartar emetic); $Bi(NO_3)_3$ (slightly sol.); $UO_2(C_2H_3O_2)_2$; $VOCl_2$; Na_2WO_4; Fe_2Cl_6; $FeSO_4$; $CoCl_2$; $NiCl_2$; H_2PtCl_6.

Of the above-named salts, $AgNO_3$, $Hg_2(NO_3)_2$, and $Hg(NO_3)_2$ were the only ones which gave any precipitation. The precipitation of mercurous nitrate appears quantitative as well as the precipitation of mercuric nitrate, while mercuric chloride gives no precipitate whatever. The precipitation of silver nitrate is only a partial one.

Among the rare earths obtainable were yttrium, samarium, gadolinium, erbium and zirconium, which, dissolved in 40 per cent. alcohol, gave with fumaric acid:

Yttrium gives no precipitate cold or hot. Samarium gives no precipitate cold or hot. Gadolinium gives no precipitate cold or hot. Erbium gives a very slight precipitate in the cold, which seems to increase somewhat on heating. Only a very small fraction, however, is thrown down. Zirconium gives a quantitative precipitation on heating.

THE COMPOSITION OF THE PRECIPITATE FORMED BY THORIUM AND FUMARIC ACID.

To determine the composition of the thorium fumarate, a quantity of pure salt was prepared by precipitating the purified thorium solution with fumaric acid, washing very thoroughly with 40 per cent. alcohol and drying. The salt was first dried at 105° C. in an air-bath, and then to determine the point at which the salt was decomposed, the temperature was gradually raised, causing a gradual loss in weight until at 202° to 205° C. it became practically constant and no indications of decomposition were evident even at 245° to 247° C. This dried salt, however, reabsorbed moisture to a considerable extent when exposed to the air.

In order to obtain concordant results, the water was first driven

off at 105° C., collected, and weighed as atmospheric moisture. For this purpose a large tin can, provided with a thermometer, was placed upon the combustion furnace, and the tube passed through in the reverse position. Air was passed through the tube and the temperature maintained at 105° for four hours; the absorption tube was weighed, the can removed and the combustion made in a current of oxygen. The water obtained in this was calculated as water of composition. The residue left in the boat should be thoria, and was weighed as such.

A number of combustions made in the above manner gave no constant results for hydrogen, while the thorium-carbon ratio was practically 1:4 as is seen from these results:

	ThO_2.	CO_2.	Ratio.
I.....	0.1319	0.0883	1 : 4.01
II.....	0.1606	0.1086	1 : 4.05

The above ratios were calculated from the thoria just after removal from the furnace. After the combustion had been completed and the boat (containing the thoria) weighed, it was placed in a platinum tube and heated with a blast-lamp for ten or fifteen minutes. White fumes were given off, and the thoria decreased in weight to the extent of several milligrams. These fumes do not condense, but if made to pass through alcohol they are partially absorbed, and from this solution a very slight precipitate can be thrown down with ammonia. The losses were:

0.1606 gram thoria lost on ignition 0.0039 gram.
0.1147 gram thoria lost on ignition 0.0036 gram.
0.1403 gram thoria lost on ignition 0.0053 gram.
0.1641 gram thoria lost on ignition 0.0054 gram.

Being under the impression that this loss was incurred by the coprecipitation (by fumaric acid) with thorium, of some compound, which on ignition with the blast yielded a volatile oxide, it was thought advisable to prepare a quantity of thorium fumarate from thorium which had been precipitated with fumaric acid and thoroughly ignited. This was done in the following way: The pure thorium solution was precipitated in the usual way with fumaric acid, and ignited for a period of one and one-half hours in the strongest heat that could be obtained from a blast-lamp. The thoria was again brought back into solution after many evaporations with concentrated sulphuric acid, precipitated with ammonia,

filtered, redissolved in nitric acid, evaporated to dryness, taken up in water and reprecipitated with fumaric acid, thoroughly washed, and dried.

Combustions were then made on this compound as before:

	ThO_2.	CO_2.	Ratio.	Loss on ignition.
I.....	0.1870	0.1270	1 : 4.07	0.0066
II.....	0.2434			0.0073

The same white fumes were driven off on ignition with the blast, causing a corresponding decrease in the weight of thoria left after combustion.

To learn whether the white fumes were a carbon-containing compound or not, the platinum tube was connected to the combustion furnace and then heated with a blast. No increase in weight was obtained in the soda-lime tube, showing the absence of carbon, but an increase, slightly greater than the loss in weight of thoria, was found in the water-absorption tube (pumice and sulphuric acid).

To find out whether the fumaric acid employed was pure and free from any non-volatile substance, several portions were burned at a gentle heat in a Bunsen flame; no residue was left. A combustion of the acid was also made giving:

	Calculated.	Found.
H	3.44	3.42
C.....	41.38	41.302

The fumaric acid was pure, and the white fumes obtained by the ignition of the thorium fumarate are as yet unaccounted for. These white fumes, however, will be made the subject of a separate investigation. The only conclusion to be drawn from the above work is that the thorium and fumaric acid react molecule for molecule. It is not supposed that the unsaturated valences in the fumaric acid play any part in the reaction, but rather that fumaric acid is of just the proper strength to throw out the very feebly basic thorium.

MONAZITE ANALYSES.

To test the application of the fumaric acid to the analysis of monazite sand, three samples were procured: two Brazil sands, and one from North Carolina,[1] and to check the results obtained,

[1] It was through the kindness of Professor Baskerville that we secured this sample of North Carolina sand.

two of the best known methods, the thiosulphate and ammonium oxalate separations, together with a third,—a combination of the thiosulphate and oxalate—were employed.

A description of the methods used is as follows:

Ammonium Oxalate Separation.—About 1 gram of the sand, ground to an impalpable powder, was weighed out into a platinum vessel, covered over with 15 to 20 cc. concentrated sulphuric acid, and evaporated on an asbestos board until fumes were no longer driven off. More sulphuric acid was added, and this repeated several times until the conversion of the phosphates into sulphates was complete.

This mass was then projected in very small quantities into about 700 cc. water at 0° C. with constant agitation (the temperature was not allowed to rise above 2° C.). This was allowed to stand several hours with frequent stirring, was filtered and washed.[1] The filtrate was then nearly neutralized with dilute ammonia (1 : 20) and 50 cc. of a cold saturated solution of oxalic acid added (for each gram of ore taken), stirred well, and allowed to stand After the heavy white precipitate had settled completely, the solution was filtered, washed, and the precipitate washed into a 400 cc. beaker, using a cold saturated solution of ammonium oxalate for the purpose. After making the volume of ammonium oxalate equal to about 50 cc. the beaker was placed on a water-bath, covered with a watch-glass, and digested for one and one-half hours with occasional stirring. This was then diluted to 300 cc. and allowed to stand over night, filtered (filtrate A), and washed. The residue was again subjected to the treatment with ammonium oxalate, etc., etc., and filtered (filtrate B).

Filtrates A and B were combined and precipitated by a large excess of ammonia, heated to boiling, filtered, and the thorium hydroxide dissolved off the filter in hot dilute nitric acid; evaporated to dryness, the residue taken up in water and precipitated with oxalic acid. This precipitate of thorium oxalate, which still contained some impurity, was again treated with ammonium oxalate as before (one treatment), precipitated with an excess of ammonia, converted into the oxalate, ignited and weighed as thorium dioxide.

[1] Preliminary experiments showed that no metals precipitable by hydrogen sulphide were present, so this part of the process was omitted.

Thiosulphate Method.—The mineral was decomposed and brought into solution as before, and precipitated with oxalic acid. The precipitate of oxalates was washed into a beaker and treated with a strong solution of caustic potash (about 25 cc.); heated to boiling (this converts the oxalates into hydroxides which are then quite soluble in acids), diluted, and filtered; washed thoroughly and dissolved off the filter in hot dilute hydrochloric acid (1:1); evaporated to dryness to free from acid, taken up in 75 to 100 cc. water and 15 cc. of a saturated solution of sodium thiosulphate added, and heated to boiling (this precipitates nearly all the thorium together with a trace of impurity and considerable sulphur); filtered (precipitate A), and the filter set aside for subsequent filtration. The filtrate was precipitated by an excess of ammonia, filtered, washed, dissolved in hydrochloric acid, evaporated to dryness, taken up in water and reprecipitated with thiosulphate as before. This was filtered through the paper containing precipitate A. The precipitation with thiosulphate was repeated, in the successive filtrates, as long as a precipitate was obtained (usually a third precipitation extracts the thorium completely).

The combined precipitates of thorium thiosulphate were washed completely, then dried and ignited. The ignited mass was fused several times with potassium bisulphate, taken up in water and a few drops of hydrochloric acid, and precipitated with oxalic acid. These oxalates were converted into the hydroxides as before, dissolved in hydrochloric acid, evaporated to dryness, taken up in water and reprecipitated with sodium thiosulphate; filtered, washed, dried and ignited. This was again fused with bisulphate, dissolved in water and a few drops of hydrochloric acid, and precipitated with oxalic acid; filtered, washed, ignited and weighed.

It was necessary to fuse the thoria several times with bisulphate to get it all into solution.

Combination Method.—Inasmuch as the methods just described are very lengthy and involve very troublesome processes, such as the repeated digestion of a large bulk of oxalates with ammonium oxalate or the repeated fusions necessary in the thiosulphate method, it was found very convenient to make a combination of the two. Another point, well worth mentioning, and shortening the process greatly, is the conversion of the thorium thiosulphate

back into the nitrate without ignition and repeated fusions. This is very easily and quickly done by washing the precipitate of thorium thiosulphate into a beaker with water, adding 20 to 25 cc. of a strong solution of caustic potash and heating to boiling. The thorium is converted completely into the hydroxide, while at the same time any free sulphur is dissolved by the caustic potash. The mass then is simply brought to boiling, diluted, filtered, washed, and dissolved off the filter in dilute nitric acid.

As has been noticed, the same reagent (caustic potash) serves for the conversion of the oxalates into hydroxides which are then easily converted into the nitrates.

The combination method is as follows:

Decompose the mineral as usual and precipitate the rare earths as oxalates; filter, and wash the oxalates into a beaker; add 20 to 25 cc. of a strong solution of caustic potash and heat to boiling; dilute, filter and wash. Dissolve the hydroxides off the filter with hot dilute hydrochloric acid (1:1) and evaporate to dryness on a water-bath. Take up with water and add 25 to 30 cc. of a saturated solution of sodium thiosulphate; heat to boiling, filter and wash (precipitate A) and set the filter aside for subsequent filtration. Precipitate the filtrate with an excess of ammonia, filter, wash, dissolve off the filter with hot dilute hydrochloric acid and evaporate to dryness. Take up with water and reprecipitate with thiosulphate as before. Filter this precipitate through the paper containing precipitate A. Wash, then wash into a beaker and add 20 to 25 cc. of a strong solution of caustic potash and heat to boiling. Dilute, filter and wash. Then dissolve off the filter in warm dilute nitric acid and evaporate to dryness. Redissolve in water and precipitate with oxalic acid; filter, wash, and rinse into a beaker using a cold saturated solution of ammonium oxalate for the purpose (about 100 cc.)[1] Digest this on a water-bath for one and one-half hours (covered with a watch-glass), dilute to 300 cc. and allow to stand over night. (The undissolved residue of cerium, lanthanum, didymium, etc., is so slight that it need not be re-treated.) Filter and precipitate the thorium from the filtrate with a large excess of ammonia. Filter, dissolve in dilute nitric acid, evaporate to dryness, take up in water and precipitate the

[1] By this process the oxalate to be digested with ammonium oxalate is almost pure thorium oxalate and goes into solution very easily. Usually only the faintest residue of impurities remains after one digestion.

thorium from this with oxalic acid. Filter, wash, ignite and weigh.

The above method gives very satisfactory results and yields a white oxide of thorium.

Fumaric Acid Method.—The three methods just described are very long and tedious. In many instances the solutions must be allowed to stand over night, and the precipitations repeated several times to insure a complete separation. The minimum time required to execute any one of these methods is from five to six days.

The method about to be described has the great advantage of being extremely short, requiring only about one and one-half days after the decomposition of the mineral, and gives accurate results. The method is as follows: Decompose about 1 gram of mineral as before and precipitate the oxalates; wash, then rinse into a beaker and add 20 to 25 cc. of a strong solution of caustic potash; heat to boiling, dilute, filter and wash. Dissolve off the filter in warm dilute nitric acid (1:1) and evaporate to dryness on a water-bath. Take up in 50 cc. water, then add alcohol and water in such proportions as to make the solution 40 per cent. alcohol (dilution = about 200 cc.). Then add 20 to 25 cc. of fumaric acid (0.1 gram per 10 cc.) and heat to boiling. Filter, while still hot, through a long-stem funnel (or by suction), wash several times with hot 40 per cent. alcohol, then return precipitate and paper to the beaker and add 25 to 30 cc. of dilute hydrochloric acid (1:1); heat to boiling, dilute a very little (keep down the volume as much as possible), and filter off the paper. Wash the paper several times, then evaporate to dryness on a water-bath, shaking from time to time and washing with a few drops of water to prevent the residue from clinging to the sides of the beaker. Add about 50 cc. water (while still on the water-bath) and stir the residue loose from the bottom with a rubber-capped rod. (The carbonaceous matter from the partly decomposed fumaric acid, etc., does not interfere.) Add alcohol and water to make the solution 40 per cent. (dilution about 150 cc.), then add about 10 cc. fumaric acid and heat to boiling. Filter through a long-stem funnel, wash with hot 40 per cent. alcohol, ignite (without previous drying) in a platinum crucible, and weigh the thorium dioxide. In this method hydrogen sulphide need not be passed through the solution before precipita-

tion with oxalic acid, for, as has been shown on a preceding page, none of the metals precipitable by hydrogen sulphide interfere.

A comparison of the analyses of the three samples of sand, made by the methods described is given in the following table: Results are given in percentages of thoria.

	Methods.			
	Fumaric.	Oxalate.	Thiosulphate.	Combination.
Brazil (*a*)	2.41	2.77	2.11	2.48
	2.55	2.03	...	...
N. Carolina...	3.95	...	...	4.03
	4.02	...	...	3.76
	3.92	...	...	...
Brazil (*b*).....	2.51	...	...	2.42
	2.47	...	...	2.56

CONCLUSIONS.

1. A saturated solution of fumaric acid in 40 per cent. alcohol precipitates thorium completely from neutral solutions, to which 40 per cent. of their volume of alcohol has been added, while under these conditions the only other metals that give precipitation are zirconium, erbium, silver, and mercury.

2. This precipitation serves as an accurate and rapid separation of thorium from the other earths in monazite, and by its use the thoria can be determined in about one-third the time required by the methods now in use and with equal if not greater accuracy.

3. As the thorium-carbon ratio in thorium fumarate is 1:4, thorium and fumaric acid react molecule for molecule.

4. By the aid of a blast-lamp, white vapors are driven off from the thoria left in the boat after the combustion of thorium fumarate in a stream of oxygen (a fact as yet not explained).

5. Rare-earth oxalates and thorium thiosulphate are completely converted into the hydroxides by heating to boiling in a strong solution of potassium hydroxide, giving a convenient method for the conversion of those salts into the nitrates.

This investigation was carried out under the direction of Professor Edmund H. Miller and I wish here to express my most sincere thanks to him for his kind interest and encouragement in the work, and for the valuable assistance rendered.

Quantitative Laboratory,
May, 1902.

ACTION OF TELLURIUM AND SELENIUM ON GOLD AND SILVER SALTS.

By R. D. Hall and Victor Lenher.

Received June 16, 1902.

HISTORICAL.

That metallic tellurium and selenium act as reducing agents upon solutions of gold and silver salts has been known since the early part of the last century, still their action has not been studied quantitatively.

N. W. Fischer[1] found that tellurium acts as a reducing agent on salts of gold, silver, platinum and palladium in solution, the reduction being incomplete in all cases, and that its action on gold solutions is the most rapid, the tellurium after a short time becoming coated with metallic gold, stopping all further action even at a high temperature. Fischer states that the action of tellurium on silver nitrate in solution is slower than on a gold solution, and that the black powder which remains is not silver but a union of tellurium and silver, each in the lowest state of oxidation. He also observes that selenium reduces a gold solution at a high temperature, the action then being the same as that of tellurium while silver and the remaining metals are not reduced.

Parkham[2] found that red selenium is blackened in a solution of silver nitrate, some flakes of selenious acid being formed at the same time; after the latter has been removed by sodium hydroxide the black powder which remains contains both selenium and silver in quantity but no unchanged selenium is visible under the microscope. He notes that tellurium in a silver nitrate solution gives a black precipitate which shows no metallic luster under pressure. After digesting tellurium for four days with an excess of a saturated silver nitrate solution he obtained a precipitate, which appeared homogeneous under the microscope, contained both tellurium and silver and no tellurous acid, and concludes that if metallic silver is precipitated by tellurium then under these conditions nearly all of the tellurium should be in solution. He analyzed neither of the precipitates but he found that selenium in a copper solution gives a precipitate which analyzed for Cu_2Se

[1] Pogg. *Ann.*, 12, 502.

[2] *Chem. Centrbl.*, 33, 813.

and that tellurium in a copper solution gives, according to conditions, Cu_2Te or CuTe, and because of this he concludes that selenium in silver solutions forms silver selenide, Ag_2Se, and that tellurium in silver solutions precipitates Ag_2Te, the telluride of silver.

Sendersens[1] found that selenium reduces a boiling solution of silver nitrate, either dilute or concentrated, with the formation of silver selenide and selenium dioxide. When the reaction was carried out in a closed tube he obtained a blue color which he thought indicated the formation of nitrogen pentoxide. The action of tellurium on a silver nitrate solution was found to be less rapid than that of selenium at 100° but similar to it; also at ordinary temperatures both metals reduce silver nitrate, the action being slow but complete.

PROCEDURE.

The following investigation was undertaken to find out whether gold and silver are precipitated from solutions of their salts by elementary tellurium and selenium. Pure tellurium and selenium were used. They were ground to a powder in an agate mortar and weighed quantities, usually about 0.1 gram, of them kept in contact with the solution of gold or silver for a definite length of time under definite conditions. The precipitate obtained was collected on a Gooch filter, dried at 100° in an air-bath and weighed; the precipitate was usually tested for either metal that it might contain and in some cases both the precipitate and the solution were analyzed. In most cases solutions containing known quantities of silver and gold were used, so that all the data necessary for an analysis was the determination of the amount of these metals remaining in the solution.

TELLURIUM IN GOLD SOLUTIONS.

In preliminary experiments on the reducing action of tellurium on solutions of gold chloride, considerable difficulty was first experienced in obtaining results consistent with the equation

$$3Te + 4AuCl_3 = 3TeCl_4 + 4Au,$$

since when tellurium is brought in contact with a gold solution the gold is apt to deposit as a coating on the tellurium, protecting it

[1] *Compt. rend.*, 104, 175.

from all further action, a fact also noted by Fischer. This was in part obviated by grinding the tellurium to an impalpable powder and even when this was done the tellurium was apt to mass in little balls which it was necessary to crush with a glass rod in order to bring all of the tellurium in contact with the gold solution. That some tellurium not infrequently escaped contact with the gold solution was shown by extracting the precipitate with such solvents as sulphur monochloride and nitric acid. None could be dissolved, showing that the tellurium present was completely enclosed by the gold; but when the precipitate was dissolved in *aqua regia,* the nitric acid evaporated off and the tellurium and gold precipitated with sulphur dioxide and this precipitate either tested for tellurium by the above solvents or by fusion with potassium nitrate, invariably where the weight of the precipitate was below that required by the above equation, tellurium could be detected.

It is not necessary that the gold chloride solution should contain more gold than is required by the reaction, for if a large excess of gold solution is used the results are the same, while if an insufficient supply is used it is entirely bleached, all of the gold being deposited. The action of tellurium on gold in solution is fairly rapid; warming a few minutes will bring down sufficient gold to color the precipitate a decided yellow, yet time is a considerable factor in bringing about complete precipitation, from two to three hours being necessary with continued heating, or several days at room temperatures. The only conditions to be observed, in order to obtain quantitative precipitation of the gold by the tellurium, are sufficient time and the direct contact of all the tellurium with the gold solution.

Experiment 1.—0.1010 gram of tellurium gave 0.2125 gram of gold; the theory, for total precipitation of the gold by the tellurium according to the equation given, requires 0.2091 gram. The gold solution used contained 0.4346 gram of gold and was in contact with the tellurium for three hours and was boiled continuously during that time. No test for tellurium could be obtained in the precipitate either before or after dissolving in *aqua regia.*

Experiment 2.—0.1099 gram of tellurium gave 0.2257 gram of precipitate; the theory requires 0.2243 gram. The gold solution

contained 0.2351 gram of gold and was in contact with the tellurium for six days at room temperature. The precipitate contained no tellurium.

Experiment 3.—0.0789 gram of tellurium gave 0.1642 gram of gold; the theory requires 0.1635 gram. The precipitate gave no test for tellurium either before or after dissolving in *aqua regia.*

SELENIUM IN GOLD SOLUTIONS.

The selenium used was prepared from sublimed selenium dioxide by precipitation with sulphur dioxide in the presence of hydrochloric acid. The selenium was dried, fused, and ground to a fine powder. The fused variety of selenium does not reduce a solution of gold chloride at room temperature. One experiment was made allowing the selenium to remain in contact with the gold solution for three months at room temperature with no visible action. At the boiling temperature the action is nearly as energetic as that of tellurium and is analogous to it, being expressed by the reaction

$$3Se + 4AuCl_3 = 3SeCl_4 + 4Au.$$

The same difficulties were encountered with the selenium as with the tellurium and were overcome in the same way. From six to eight hours of continued boiling are necessary to insure complete precipitation, or better from two to three days at a temperature of from 70° to 80°.

Experiment 1.—0.0712 gram of selenium gave 0.2345 gram of gold, the calculated being 0.2336 gram.

Experiment 2.—0.1058 gram of selenium gave 0.3455 gram of precipitate; the theory requires 0.3470 gram. The amount of gold contained in the solution was 0.4346 gram and it was in contact with the selenium for three days at a temperature of about 80°. The precipitate gave no test for selenium after dissolving and reprecipitating.

Experiment 3.—0.1502 gram of selenium in a solution of gold chloride boiled for five hours gave 0.4892 gram of gold; the amount required by the theory is 0.4926 gram; the precipitate gave no test for selenium.

TELLURIUM IN SILVER SOLUTIONS.

The first salts used were ammoniacal solutions of the nitrate and

the chloride of silver. In both cases the solutions were reduced by the tellurium, slowly in the cold and more rapidly if heated, yet tellurium digested with silver nitrate solution for a long time would not completely go into solution leaving metallic silver. Where an ammoniacal solution of silver nitrate was used the weight of the precipitate and the amount of silver in the precipitate, was in excess of that required for silver telluride. The amount of silver and tellurium as determined by analysis did not add up to the total weight of the precipitate and in several cases small plates of metallic silver were formed. On repeating the experiment with no tellurium present it was found that when silver nitrate stands in contact with ammonia for some time or is warmed with it a deposit is formed which is insoluble in ammonia. This deposit is probably silver nitride, but when the solution is boiled or kept warm several days the precipitate contains plates of metallic silver. In subsequent experiments the silver nitrate solution was used without ammonia and the silver tellurite formed was removed by washing the precipitate with ammonia.

When silver chloride in ammonia was used, it was allowed to stand in contact with the tellurium at room temperature or only slightly warmed, an excess of ammonia always being present to keep the silver chloride in solution. When the nitrate was used a greater range of temperature was possible and the solution was either boiled continuously or kept at a temperature of about 80° for a long time. At the end of the experiment the precipitate was collected on a Gooch filter, washed several times with ammonia to remove any silver tellurite and then with water. In this way results were obtained which agree very well with those required by the equation

$$4AgNO_3 + 3Te = 2Ag_2Te + Te(NO_3)_4$$

where the nitrate of silver is used, and

$$4AgCl + 3Te = 2Ag_2Te + TeCl_4$$

where the chloride in ammonia was used. Either the chloride or the nitrate of tellurium would be decomposed by water and would then react with more silver nitrate or chloride to form the tellurite of silver.

Experiment 1.—0.1099 gram of tellurium gave 0.1848 gram of precipitate; the calculated amount of silver telluride was 0.1978

gram. The solution contained 0.4320 gram of silver as the chloride and was in contact with the tellurium for eight days.

Experiment 2.—0.1005 gram of tellurium in a solution of silver chloride containing 0.2160 gram of silver gave 0.1843 gram of precipitate, that required for silver telluride being 0.1809 gram; the time of the experiment was ten days.

Experiment 3.—0.0994 gram of tellurium in a solution of silver chloride containing 1.0800 grams of silver gave 0.1767 gram of precipitate, the calculated for silver telluride being 0.1789 gram. The time of the experiment was three months, and during that time it was kept in a warm place and ammonia added occasionally.

Experiment 4.—0.1018 gram of tellurium in a solution of silver nitrate which contained 2.0601 grams of silver gave 0.1871 gram of precipitate, that required for silver telluride being 0.1841 gram. The silver remaining in the solution was determined as the chloride and found to be 1.9404 grams which would make the loss from the solution or the amount of silver in the precipitate as 0.1192 gram and the amount of tellurium in the precipitate 0.0693 gram. The calculated amount of silver in 0.1871 gram of the telluride is 0.1178 gram and the tellurium 0.0693 gram.

The low results in the above series of experiments can be attributed in a large measure to small amounts of tellurium which were so thoroughly enclosed in the mass that they could not be brought to enter into the reaction.

An attempt was made to prepare silver telluride in order to study its properties and compare it with the precipitate obtained from the reduction of the silver solution by tellurium. An excess of aluminum was fused with tellurium and hydrogen telluride evolved from this by treatment with dilute hydrochloric acid. The hydrogen telluride was passed into an ammoniacal solution of silver nitrate in an atmosphere of carbon dioxide to prevent any decomposition of the hydrogen telluride by the oxygen of the air. This gave a black precipitate which was washed repeatedly with water, then dried in an air-bath at 105°. Analysis showed the substance to contain 22.3 per cent. tellurium and 77.3 per cent. of silver while the theory for silver telluride requires 37.1 per cent. of tellurium and 62.9 per cent. of silver. The silver in another sample, prepared in a similar way, was determined by heating the substance in a boat in a current of chlorine gas; the tellurium distilling off as the tetrachloride and the silver chloride remaining

was weighed. The per cent. of silver obtained in this way was 75.4.

The substance thus prepared fused without loss of tellurium as was indicated by the absence of fumes, to a porous mass which cut with a metallic luster. It was acted on by sulphur monochloride, forming tellurium tetrachloride; it reduced a gold solution, depositing metallic gold, but no action could be observed with a silver solution.

The action of hydrogen telluride on silver nitrate may be explained by the decomposition of hydrogen telluride in presence of silver nitrate into nascent hydrogen and tellurium and these then would reduce the silver solution, the first causing metallic silver to be deposited while the latter would give rise to silver telluride, and this would explain the high percentage of silver.

Silver tellurite was prepared by adding potassium tellurite (obtained by fusion of equivalent weights of tellurium dioxide and potassium carbonate) to a silver nitrate solution; it was dried at 105° and as obtained was a light yellow powder, fairly permanent in the light. Analysis gave 54.95 per cent. of silver, while the formula Ag_2TeO_3 requires 55.17 per cent. This silver tellurite was reduced by heating it in a porcelain tube to the highest temperature obtainable in the blast-lamp and passing a current of dry ammonia over it for one hour. At the temperature used, tellurium alone would have entirely distilled from the boat. 1.1990 grams of the silver tellurite were used and 1.0440 grams of residue obtained; the weight required for silver telluride from the amount of tellurite used is 1.0517 grams. The compound obtained by the reduction of the tellurite was analyzed by heating in a current of chlorine. 0.2276 gram gave 0.1908 gram of silver chloride or 62.65 per cent. of silver, the calculated for silver telluride being 62.97 per cent. Another sample of silver tellurite was reduced in carbon monoxide under similar conditions and the telluride formed was similar in all respects to that obtained by reduction in ammonia.

The silver telluride obtained by the reduction of silver tellurite had a strong metallic luster, did not tarnish readily, was harder than tellurium, was brittle but not brittle enough to be ground to a powder; it was broken up as finely as possible and treated with

sulphur monochloride, gold chloride solution and silver nitrate solution. Sulphur monochloride acted on it slowly to form tetrachloride; the gold solution was bleached and the silver telluride became coated with gold. 0.2995 gram was boiled with a solution of silver nitrate for eight days; at the end of that time the solution gave no test for tellurium while the particles had lost none of their luster, showing them to be entirely unacted on.

Brauner[1] synthesized silver telluride by fusion of silver in a current of tellurium. He obtained a crystalline mass of metallic luster having approximately the composition Ag_2Te.

In an article on the "Naturally Occurring Telluride of Gold" by one of us[2] specimens of sylvanite, calaverite, coloradoite, kalgoorlite, and nagyagite were treated with a gold solution, and in all cases metallic gold was obtained. Recently some excellent specimens of krennerite, hessite and more specimens of sylvanite and calaverite were obtained, and as specimens of some of these minerals were not at hand at the time of the previous investigation their action on solutions of gold chloride and silver nitrate was now tried. The minerals examined were:

One specimen calaverite, Keystone, Boulder Co., Colo. (this was one of the original specimens of Genth).

One specimen calaverite and one of sylvanite from Cripple Creek, Col.

Three specimens hessite from Boles, Siebenburgen, Hungary.

One specimen hessite from Tombstone, Arizona.

One specimen krennerite, West Side Mine, Cripple Creek, Col.

One specimen krennerite, Boles, Siebenburgen, Hungary.

All of these minerals reduced gold chloride solution, becoming coated yellow and where a small quantity of solution was used bleached it, agreeing with the previous results. The hessite was without visible action on the silver nitrate solution even when boiled in it; one specimen of krennerite and one of sylvanite gave a small amount of black powder similar to that obtained from tellurium in silver nitrate solution. Hessite is telluride of silver, which as we have seen is without action on silver solutions, while the others contain both silver and gold with the tellurium, or gold with tellurium, from which it would seem that while the combina-

[1] *J. Chem. Soc.*, **55**, 388

[2] This Journal, **24**, 355.

tion of silver with tellurium is without action on silver nitrate solution that of gold with tellurium reduces silver nitrate.

In the same article reference was made to the action of tellurium on silver nitrate solution, and conclusions stated which in the light of the facts then at hand seemed correct. It was stated that the action of tellurium on silver solutions is similar to that on gold solutions, though not as complete, metallic silver being formed. The results in this later work show that tellurium in silver solutions forms the telluride of silver and not metallic silver. The error in the former statements arose from the use of ammonia in the solution while it was in contact with the tellurium; it was subsequently found that silver nitrate solution standing for a long time with ammonia, or being heated with it, gives a deposit which contains metallic silver.

SELENIUM IN SILVER SOLUTIONS.

Selenium reduces a solution of silver nitrate or of the chloride in ammonia, either in the cold or on heating. The action is less rapid than that of tellurium but similar to it, a close approximation to the selenide of silver being formed. Parkham's statement that a precipitate of selenium dioxide is formed is obviously incorrect as he used aqueous solutions, and selenium dioxide is readily soluble in water. The precipitate that he obtained must have been silver selenite. Sendersen's experiment of heating the solution in contact with the selenium in a closed tube was repeated; no difference could be detected in the outcome of the reaction, and no blue coloration was observed.

Experiment 1.—0.1012 gram of selenium in a solution of silver nitrate for eight days gave 0.2513 gram of precipitate, the theory requiring 0.2497 gram.

Experiment 2.—0.1047 gram of selenium in a solution of silver chloride containing 0.4320 gram of silver, gave 0.2550 gram of precipitate, the calculated for silver selenide being 0.2590 gram.

Experiment 3.—0.1012 gram of selenium in a solution of silver nitrate containing 2.4157 grams of silver gave 0.2468 gram of precipitate, the theory for silver selenide being 0.2497 gram. After the removal of the precipitate the solution contained 2.2370 grams of silver which would make the precipitate contain 0.1785 gram of silver and 0.0683 gram of selenium, the calculated amounts for

0.2468 gram of silver selenide being 0.0666 gram of selenium and 0.1802 gram of silver.

The precipitate obtained in Experiment 2 was treated with a solution of gold chloride and reduced it nearly as well as does elementary selenium. The fact that both the telluride and the selenide of silver reduce gold chloride suggested an investigation of the action of the sulphide of silver on solutions of silver and gold. Silver sulphide was prepared by passing hydrogen sulphide into a solution of silver nitrate made alkaline with ammonia, the precipitate washed, dried in an air-bath and then washed with carbon bisulphide to remove any excess of sulphur. A sample of silver sulphide prepared in this way was boiled with a solution of silver nitrate for seven days and the solution tested for sulphur without any trace being found to be present. The silver sulphide reduced gold chloride solution to metal, readily on warming but only slightly in the cold.

CONCLUSIONS.

Tellurium reduces a gold chloride solution completely to metallic gold either in the warm or in the cold and the only difficulties so far as quantitative precipitation is concerned are mechanical ones. The action of tellurium on silver salts in solution is to reduce them with formation of the telluride of silver, which is still a reducing agent as it throws gold out from solution. The behavior of the product obtained is, in all respects, similar to that of the telluride of silver obtained by the reduction of silver tellurite and to that of the native mineral itself.

The action of selenium is similar to that of tellurium but is not as energetic. Selenium reduces silver solutions in the cold, but has no action on gold solutions unless heated nearly to boiling, the action then being fairly rapid and complete. With silver solutions selenium forms silver selenide wnich resembles silver telluride in being a reducing agent to solutions of gold salts, both of them being similar to the sulphide of silver in this respect.

UNIVERSITY OF WISCONSIN,
MADISON, WIS.

THE APPLICATION OF POLARIMETRY TO THE ESTIMATION OF TARTARIC ACID IN COMMERCIAL PRODUCTS.[1]

BY EDGAR B. KENRICK AND FRANK B. KENRICK.

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IN comparing the optical rotation of the sugars with that of active substances generally, we meet with one great point of difference. While concentration and the presence of foreign substances play only a subordinate part in the rotation of the former, so that their influence may usually be ignored, in the case of other active substances the effects of these disturbing factors may be extremely complex. The object of the present research has been to investigate the influence of various commonly occurring substances on the rotation of tartaric acid, and, by taking these effects into account, to devise methods for the polarimetric estimation of tartaric acid in its chief commercial compounds.

Tartaric acid, in aqueous solution, rotates the plane of polarization to the right. Strong acids slightly decrease this rotation. The rotation of the salts is, in general, a little greater than that of the free acid, and, in case of dilute solutions, is independent of the nature of the base.

The facts, so far, are in accordance with the hypothesis of electrolytic dissociation. There are, however, a number of substances which exert a much greater effect on the rotation, and whose action is best explained on the assumption of the formation of complex molecules. As early as 1837 Biot observed that borax increased the rotation of tartaric acid, and subsequently Gernez[2] and others pointed out that the acids of arsenic, antimony, molybdenum and tungsten, also the salts of beryllium and uranium, exercised a similar influence.

The present writers, besides confirming the observations of the earlier experimenters, have studied the influence of a number of other elements on the rotation of tartaric acid. The following is a summary of the conclusions arrived at, the results given being the effects noted, except where otherwise stated, in the presence of ex-

[1] A preliminary note on this subject was published in the Appendix to Bulletin No. 65 (p. 157) of the Bureau of Chemistry, U. S. Department of Agriculture. In the present paper fuller details are given, and some slight changes have been made in the methods of analysis.

[2] *Compt. rend.*, 105, 803 (1887).

cess of ammonia. Where the effects are described as small, the slight changes observed in the rotation were often within the limits of experimental error.

The Alkali Metals.—Lithium, sodium, potassium and caesium were found to have a small effect only on the rotation.

Copper and Silver.—These metals, the former in the presence of potassium cyanide, had practically no effect on the rotation.

The Alkaline Earth Metals.—Although the tartrates in this group are nearly insoluble, small quantities of the salts of calcium, strontium and barium may be added to an ammoniacal solution of tartaric acid and the solution polarized before the tartrates have time to crystallize out. It was found that, while calcium exercised an insignificant effect only, strontium and barium lowered the rotation.

Magnesium, Zinc and Cadmium.—The first two had a small effect only; cadmium increased the rotation.

Boron and Aluminum.—Boracic acid (in alkaline solution) lowered the rotation; compounds of aluminum had the opposite effect.

Tin and Lead.—Both stannous and stannic salts increased the rotation; lead diminished it.

Arsenic, Antimony and Bismuth.—These all lowered the rotation in the presence of an excess of ammonia. It has long been known that a solution of tartar emetic has a much higher rotation than a solution containing the equivalent quantity of tartaric acid. The authors found that when ammonia is added in excess to an aqueous solution of tartar emetic part only of the antimony is precipitated. The filtrate then has a *lower* rotation than an equivalent solution of ammonium tartrate. Similarly, if an ammoniacal solution of cream of tartar is shaken up with excess of antimony oxide, a certain quantity of antimony passes into solution. The solution so obtained has a lower rotation than the original cream of tartar solution, its rotation corresponding, in fact, to that of the filtrate referred to above—provided, of course, the solutions of cream of tartar and tartar emetic are made of equivalent strength.

Manganese.—Manganese sulphate, added to an ammoniacal solution of tartaric acid and made up to volume with freshly boiled water, gives a colorless solution, and the rotation of the tartaric

acid is practically unaffected. But if this mixture is exposed to the air it very quickly turns to a deep, reddish brown, and a considerable decrease in the rotation takes place.

Iron, Nickel and Cobalt.—Iron and nickel compounds increase the rotation, while salts of cobalt have a lowering effect. Owing to the fact that these metals give deeply colored solutions with ammoniacal tartaric acid, only very small quantities of the salts can be added to the solutions for polarization.

Non-Metallic Radicals.—The majority of the common acids have little or no effect on the rotation of tartaric acid. Observations were made on the following: Chlorides, bromides, iodides, cyanides, chlorates, carbonates, nitrates, phosphates, sulphates, acetates, oxalates, and citrates.

As in the case of antimony and certain other elements, the magnitude of the effect produced by molybdic acid was found to depend very largely on whether the solution was acid, neutral, or alkaline.

Considering the common occurrence of iron and aluminum in commercial products, it is unnecessary to emphasize the importance of a knowledge of the effects of these metals in estimating tartaric acid by the polariscope. From the fact that the alkaline tartrates dissolve the hydroxides of iron and aluminum, even in the presence of ammonia, it might be anticipated that these metals would influence the optical activity of tartaric acid by the formation of complex molecules. It was found indeed that even the comparatively small quantities of iron and aluminum, such as occur as impurities in the superphosphates employed in baking-powders, exerted sufficient influence to invalidate determinations based on direct measurements of the rotation of the tartaric acid in the mixture (Appendix 27 and 40).

The chief commercial products containing tartaric acid as an essential ingredient are: cream of tartar, cream of tartar "compounds", tartar baking-powders and certain pharmaceutical salts and mixtures. The latter include not only the official preparations of the different pharmacopoeias, but also the proprietary effervescing remedies, etc. These different materials may be conveniently classed into three main groups, corresponding to the methods of analysis described below.

Group I.—Tartaric acid and mixtures containing tartaric acid and calcium tartrate, but no other optically active material, or any substance, such as iron or aluminum, capable of modifying the rotation of tartaric acid in ammoniacal solution. To this class belong Rochelle salt, potassium tartrate, cream of tartar, and many of the effervescing preparations of the pharmacopoeias.

Group II.—Mixtures containing both tartaric acid and sugar. Some of the officinal effervescing compounds and most of the similar patent preparations fall into this division.

Group III.—Mixtures containing tartaric acid with one or more modifying agents, or traces of optically active substances. This group comprises materials of which alum is an ingredient, mixtures containing traces of iron or aluminum, and those of which starch is a constituent. Consequently all tartar baking-powders and mixtures of cream of tartar with cream of tartar substitutes are included in this group. For apart from the fact that the latter are liable to contain iron and alumina, the authors found that the starch mixed with baking-powders[1] and superphosphates almost invariably contained traces of active substances soluble in cold water (Appendix 87-101).

METHODS OF ANALYSIS.

In the following section, working details of the several methods are given, corresponding to the classification indicated above. In the Appendix (109-112) examples of the different methods will be found.

Group I.—The method employed in the analysis of materials of this group is based on the fact that in the presence of excess of ammonia the rotation of the solution is proportional to the concentration of the tartaric acid, and is independent of the other bases and acids present.

(1) *The Tartrates Present are Completely Soluble in Dilute Ammonia.*—A weighed quantity of the substance containing not more than 2 grams tartaric acid is placed in a 50 cc. measuring flask, moistened with 3 or 4 cc. of water, and concentrated ammonia (sp. gr. 0.924) added in quantity sufficient to neutralize all acid that may be present and leave about 2 cc. in excess. The

[1] There are, however, a few tartar baking-powders on the market which are entirely free from starch. These may be classed in Group I.

actual amount of the excess is not of importance, but a greater quantity than 2 cc. of free ammonia should be avoided. The solution is then made up to 50 cc. with water, filtered, if necessary, through a dry filter, and the rotation read in a 200 mm. tube.

The amount of tartaric acid ($C_4H_6O_6$) in grams (y) in the material taken is given by the formula

$$y = 0.00519x,$$

where x is the rotation in minutes.

(2) *The Mixture Contains Insoluble Calcium Tartrate.*—In this case proceed as follows: Treat 2 grams of the sample (or an amount containing not more than 2 grams of tartaric acid) in a small beaker with 30 cc. water and 20 drops concentrated hydrochloric acid. Heat gently till both the potassium and calcium tartrates have passed into solution, and then, while still hot, add 4 cc. concentrated ammonia (or enough to produce an ammoniacal smelling liquid) and about 0.2 gram sodium phosphate dissolved in a little water. Transfer to a 50 cc. measuring flask, cool, make up to the mark with water, filter through a dry filter, and polarize the filtrate in a 200 mm. tube. The tartaric acid is calculated by the formula given under (1).

The precipitation of the calcium by sodium phosphate is not absolutely necessary, but, when this is not done, in cases where the proportion of calcium tartrate in the sample is high, there is a great tendency for the calcium tartrate to crystallize out from the ammoniacal solution before the reading is made.

The tartaric acid present as bitartrate of potash may be determined by proceeding as in (1), the calcium tartrate being practically insoluble in cold ammonia solution.

The tartaric acid in the calcium tartrate may be obtained with sufficient accuracy for most purposes from the difference between the results in (1) and (2). If more exact results are required, the residue insoluble in ammonia in (1) may be dissolved in a little hydrochloric acid, and treated as above with sodium phosphate and ammonia.

It may be noted that the method given below under Group III, is applicable to this group also, but in most cases the course described above will be found more simple.

Group II.—The method of analysis for substances of this group

is essentially the same as the one just described, but takes into account the presence of sugar in the mixtures. In ammoniacal solutions containing both tartaric acid and sugar, the rotation of each is unaffected by the presence of the other (Appendix 45-46), and consequently the rotation of the tartaric acid may be obtained by subtracting from the total rotation the part due to the sugar. The cane-sugar may be determined by Clerget's method, but in carrying out the process the additional precautions described below must be observed.

Although magnesium sulphate, even in comparatively large proportions, has but little effect on the rotation of solutions of sugar and of tartaric acid alone, it is a curious fact that the rotation of these two substances when present together is considerably decreased by the addition of magnesium sulphate (Appendix 22 and 67). In "effervescing magnesium sulphate", and in other mixtures where magnesia is present, it is therefore necessary to precipitate the magnesium by means of sodium phosphate and ammonia before making the polarimetric readings.

In carrying out the inversion of cane-sugar, moreover, it must be remembered that in order to effect complete inversion in ten minutes, without further decomposing the products of hydrolysis, a fairly definite concentration of free hydrochloric acid is required, and that when salts of weak acids (such as citric and tartaric) are present, it is only the hydrochloric acid added over and above the amount necessary to completely set free all these weak acids that is to be considered capable of effecting the inversion in the prescribed time. The difficulty of finding the point where hydrochloric acid is free in the solution was overcome by the use of methyl violet as indicator. This indicator was found to be quite unaffected by citric and tartaric acids, yet sufficiently sensitive to hydrochloric acid for the purpose in hand.

It is also to be noted that in some commercial samples the sugar is already partly in the inverted condition. In such cases the reducing sugar must be determined by Fehling's process, and due allowance made for it.

(1) *Magnesium Absent.*—An amount of the sample containing not more than 8 grams of tartaric acid or 5 grams of sugar is dissolved in cold water and made up to 100 cc. (Solution *A*).

Twenty-five cc. of this solution are pipetted into a 50 cc. measuring flask with a few drops of methyl orange solution and, if alkaline, approximately neutralized with concentrated hydrochloric acid. One cc. concentrated ammonia (sp. gr. 0.924) is then put in, the flask filled to the mark, and the solution polarized in a 200 mm. tube (reading a).

To another 25 cc. of Solution A a little methyl violet solution is added, and concentrated hydrochloric acid run in from a burette till the indicator turns pale green, the amount of acid required being noted.

A third 25 cc. portion of Solution A is placed in a 50 cc. measuring flask (without methyl violet, the color of which would interfere with the polarimetric readings) and a quantity of hydrochloric acid run in equal to the amount required in the last experiment, *plus* 2.5 cc. The flask and contents are next heated to 70° C. for ten minutes, as in the ordinary Clerget process, and immediately cooled to ordinary temperature. A little methyl orange is then added and enough ammonia to turn the indicator yellow and leave about 1 cc. in excess. Finally, after making up the volume to 50 cc., and cooling to the temperature of the room, the solution is polarized in a 200 mm. tube (reading b).

The weight of sugar (z) in the amount of the sample taken is given by the formula

$$z = \frac{2(a-b)\,1.254}{142 - 0.5t},$$

where t is the temperature and a and b are the readings expressed in minutes.

The rotation of z grams uninverted sugar is $79.7z$, and the rotation (x) of the tartaric acid is consequently

$$x = 2a - 79.7z,$$

from which the tartaric acid (y) is found by the formula

$$y = 4 \times 0.00519x \text{ (see 1)}.$$

(2) *Magnesium Present.*—A solution of the substance is prepared as in (1) above (Solution A). Ten cc. of this solution are placed in a beaker and about 25 cc. of water and 4 cc. of concentrated ammonia added. If a precipitate forms, enough ammonium chloride is added to keep it in solution. The magnesium is then precipitated by sodium phosphate. Since it is desirable to keep

the bulk of the solution as small as possible, and to avoid unnecessary excess of salts in solution, the required quantity of phosphate (about 8 grams $Na_2HPO_4 10H_2O$ to every 5 grams $MgSO_4 7H_2O$) should be dissolved in a small volume of hot water (10 cc. to 8 grams phosphate) and the solution added gradually while hot. After the precipitate has completely formed it is filtered off on the filter-pump and washed with small quantities of water, care being taken not to bring the total volume to more than 100 cc. Even a fairly bulky precipitate can be sufficiently washed in this way.

The filtrate is now made up to 100 cc. (Solution *B*), and part of this solution read at once in the polarimeter (reading *c*.)

Twenty-five cc. of Solution *B* are now titrated with hydrochloric acid and methyl violet, and another 25 cc. inverted as described under (1), made up to 50 cc. and polarized (reading *d*).

The weight of sugar (z) in the substance taken is

$$z = \frac{10\,(c - 2d)\ 1.254}{142 - 0.5\,t}.$$

The rotation of the tartaric acid is, therefore,

$$x = 10c - 79.7z$$

and the weight of tartaric acid,

$$y = 4 \times 0.00519x.$$

The directions given for this method are, of course, subject to slight modification depending on the relative amount of magnesium present; in some cases, for instance, more ammonia than 6 cc. might be necessary. It may be stated, however, that the amount of free ammonia in the uninverted solution is not of much consequence, but in the inverted solution the excess should not exceed 1 cc. (Appendix 51-66).

On account of the bulk of the magnesium precipitate, and because large quantities of neutral salts affect the rotation, it is necessary to work with weaker solutions when magnesium is present. For this reason only 10 cc. of Solution *A* are taken in (2).

In the Appendix test analyses are given of some effervescing mixtures, as illustrating the methods used in Group II. It may, however, be pointed out here that the results of the analyses of commercial *granulated* effervescing preparations do not agree with

results calculated from the formulas in the pharmacopoeias. This is owing to the fact that a considerable amount of decomposition takes place in the process of manufacture. Hence tartaric acid, and all other constituents with the exception of carbon dioxide, come out higher in the analysis than in the result calculated from the formula. This consideration does not apply to the test analyses given, as in these the whole of the mixture made up was taken for analysis, and no attempt was made to imitate exactly the "granulated" commercial article.

Group III.—Direct readings of rotation in ammoniacal solution are inadmissible in analyses of the substances of this group on account of the influence of iron and aluminum on the rotation of tartaric acid, and owing to the small, but unknown, rotation of the trace of inverted starch (Appendix 27, 40, 87-101).

Accurate determinations may, however, be made in the presence of excess of ammonium molybdate in neutral solution. The latter salt not only annuls the effect of iron and aluminum, but also has the property of greatly increasing the rotation of tartaric acid, so that by its use the small rotation of the inverted starch is rendered insignificant. It is to be noted, however, that this increased rotation is very sensitive to the presence of acid and alkali, and is, moreover, modified by the presence of phosphates. It therefore becomes necessary to first remove the phosphoric acid, and then to bring the solution to a definite state of neutrality. These results are attained by the following procedure, the details of which must be strictly adhered to.

Solutions Required.—The following solutions must be prepared, but need not be made up very accurately.

Molybdate solution, 44 grams ammonium molybdate in 250 cc.
Citric acid solution, 50 grams citric acid in 500 cc.
Magnesium sulphate solution, 60 grams $MgSO_4.7H_2O$ in 500 cc.
Ammonia solution, 165 cc. ammonia (sp. gr. 0.924) in 500 cc.
Hydrochloric acid, 60 cc. concentrated acid in 500 cc.

An amount of the sample containing not more than 0.2 gram tartaric acid, not more than 0.3 gram alum and not more than 0.3 grain calcium acid phosphate is weighed into a dry flask. To this, 10 cc. citric acid and 10 cc. molybdate solution are added, and allowed to react with the substance for ten or fifteen minutes,

shaking the liquid occasionally. Next, 5 cc. magnesium sulphate solution are added and 10 cc. ammonia solution are stirred in. These solutions are all measured exactly, so that the total volume will be 35 cc. If the original substance is a liquid, room may be made for it by taking a smaller volume of stronger ammonia. After a few minutes (not more than an hour), the solution is filtered through a dry filter, a slight turbidity of the filtrate being disregarded. To 20 cc. of the filtrate, measured into a 50 cc. flask, are then added a few drops of methyl orange, and hydrochloric acid from a burette till the pink color appears (two or three drops too much or too little are of no consequence). Finally 10 cc. more molybdate solution are added to the pink solution, which now becomes colorless or pale yellow, and water to make up the volume to 50 cc. This solution, after filtering if necessary, is polarized in a 200 mm. tube.

The amount of tartaric acid in grams (y) in the weight of sample taken is given by the following formula, in which x is the rotation in minutes (Appendix 105-108).

$$y = 0.00121\,x.$$

A word of explanation may be given here with regard to the function of the citric acid in the above method. It was found that although under ordinary circumstances tartaric acid entirely prevents the precipitation of aluminum hydroxide by ammonia, this is not the case when molybdate is present, and, consequently, when the ammonia was added to the solution to precipitate the magnesium ammonium phosphate, the aluminum was simultaneously thrown down. This not only produced a liquid which was extremely difficult to filter, but the precipitate appeared to carry down a considerable quantity of the tartaric acid. The addition of citric acid prevents the precipitation of the aluminum without interfering with the formation of the magnesium phosphate; indeed, this precipitate may be ignited and used for the quantitative determination of the phosphoric acid in the sample.

It may also be mentioned in this connection that the removal of the phosphoric acid by means of molybdate in acid solution is not practicable, for when sufficient acid is added to effect this result, the molybdic acid rapidly oxidizes the tartaric acid and is itself converted into one of the blue reduction products.

The above methods cover most of the cases that occur in practice. Samples containing tartar emetic cannot, however, be analyzed by these methods (without modification), and great caution should be exercised in extending any of the methods described to cases involving the presence of foreign substances not taken into account in this paper.

APPENDIX.

In this section some of the experimental data are recorded. The readings were made mostly with a Schmidt & Haensch half-shadow instrument, graduated in degrees and minutes. A 200 mm. tube was used for the readings. The light was supplied by a flame in which sodium chlorate was heated on platinum. It was found that the readings for tartaric acid were practically independent of the temperature, and, except where otherwise indicated, the observations were made at room temperature. The rotations recorded in the following tables are expressed in minutes. In this section TH_2 stands for tartaric acid; KHT, potassium bitartrate; CaT, calcium tartrate tetra-hydrate; NH_3, ammonia of sp. gr. 0.924 (11 normal); HCl, concentrated hydrochloric acid, 9.2 normal; alum, crystallized ammonia alum.

The potassium bitartrate and calcium tartrate used in these experiments were specially prepared for this work, and found by analysis to be almost absolutely pure.

THE EFFECT OF VARIOUS SUBSTANCES ON THE ROTATION OF TARTARIC ACID IN AMMONIACAL SOLUTION.

					Rotation.
(1)	4 g. TH_2	4 cc. NH_3		in 100 cc.	193.5
(2)	4 g. TH_2	8 cc. NH_3		in 100 cc.	194
(3)	4 g. TH_2	40 cc. NH_3		in 100 cc.	193
(4)	4 g. TH_2	8 cc. NH_3	4 g. ammonium chloride	in 100 cc.	196
(5)	4 g. TH_2	8 cc. NH_3	4 g. ammonium nitrate	in 100 cc.	194
(6)	4 g. TH_2	8 cc. NH_3	4 g. ammonium sulphate	in 100 cc.	196
(7)	4 g. TH_2	8 cc. NH_3	4 g. ammonium oxalate	in 100 cc.	192
(8)	4 g. TH_2	8 cc. NH_3	4 g. lithium chloride ..	in 100 cc.	187
(9)	4 g. TH_2	8 cc. NH_3	4 g. sodium chloride ..	in 100 cc.	194
(10)	4 g. TH_2	8 cc. NH_3	4 g. sodium phosphate	in 100 cc.	188
(11)	4 g. TH_2	8 cc. NH_3	4 g. sodium acetate	in 100 cc.	186
(12)	4 g. TH_2	8 cc. NH_3	4 g. potassium chloride	in 100 cc.	197
(13)	4 g. TH_2	8 cc. NH_3	4 g. potassium bromide	in 100 cc.	194
(14)	4 g. TH_2	8 cc. NH_3	4 g. potassium iodide...	in 100 cc.	194

			Rotation.
(15)	4 g. TH_2 8 cc. NH_3	4 g. potassium cyanide. in 100 cc.	194
(16)	4 g. TH_2 8 cc. NH_3	4 g. potassium chlorate. in 100 cc.	192
(17)	4 g. TH_2 8 cc. NH_3	4 g. potassium nitrate . in 100 cc.	196
(18)	4 g. TH_2 8 cc. NH_3	4 g. potassium sulphate in 100 cc.	197
(19)	4 g. TH_2 8 cc. NH_3	1 g. caesium sulphate.. in 100 cc.	197
(20)	4 g. TH_2 8 cc. NH_3	4 g. copper sulphate + potassium cyanide in 100 cc.	196
(21)	4 g. TH_2 8 cc. NH_3	4 g. silver nitrate in 100 cc.	197
(22)	4 g. TH_2 8 cc. NH_3	4 g. magnesium sulphate in 100 cc.	194
(23)	4 g. TH_2 8 cc. NH_3	4 g. zinc sulphate..... in 100 cc.	194
(24)	4 g. TH_2 8 cc. NH_3	4 g. zinc acetate in 100 cc.	190
(25)	4 g. TH_2 8 cc. NH_3	4 g. cadmium sulphate. in 100 cc.	220
(26)	4 g. TH_2 8 cc. NH_3	4 g. boracic acid in 100 cc.	150
(27)	4 g. TH_2 8 cc. NH_3	2 g. alum..... in 100 cc.	246
(28)	4 g. TH_2 8 cc. NH_3	4 g. stannic chloride ... in 100 cc.	305
(29)	4 g. TH_2 8 cc. NH_3	4 g. stannous chloride (precipitate filtered off) in 100 cc.	233
(30)	4 g. TH_2 16 cc. NH_3	2 g. lead acetate..... in 100 cc.	83
(31)	4 g. TH_2 8 cc. NH_3	4 g. sodium arsenite ... in 100 cc.	179
(32)	4 g. TH_2 8 cc. NH_3	4 g. sodium arsenate ... in 100 cc.	185
(33)	4 g. TH_2 14 cc. NH_3	4 g. bismuth subnitrate + 6 cc. hydrochloric acid..... in 100 cc.	25
(34)	4 g. TH_2 28 cc. NH_3	4 g. bismuth subnitrate + 6 cc. hydrochloric acid..... in 100 cc.	114
(35)	4 g. TH_2 8 cc. NH_3	excess of antimony oxide in 100 cc.	177
(36)	8.86 g. tartar emetic, ammonia in excess (filtrate) . in 100 cc.		178
(37)	4 g. TH_2 8 cc. NH_3	4 g. manganese sulphate in 100 cc.	193
(38)	The same exposed to the air for a few minutes		167
(39)	4 g. TH_2 8 cc. NH_3	0.1 g. manganese sulphate after exposure..... in 100 cc.	183
(40)	4 g. TH_2 8 cc. NH_3	0.02 g. ferric chloride in 100 cc.	210
(41)	4 g. TH_2 8 cc. NH_3	0.3 g. nickel sulphate.... in 100 cc.	202
(42)	4 g. TH_2 8 cc. NH_3	0.1 g. cobalt nitrate..... in 100 cc.	189
(43)	4 g. TH_2 8 cc. NH_3	4 g. citric acid..... in 100 cc.	192
(44)	4 g. TH_2 16 cc. NH_3	4 g. citric acid..... in 100 cc.	194
(45)	4 g. TH_2 8 cc. NH_3	4 g. cane-sugar in 100 cc.	508
(46)	8 cc. NH_3	4 g. cane-sugar in 100 cc.	314
	Difference between (45) and (46) due to 4 g. TH_2		194

THE RELATION BETWEEN THE ROTATION AND CONCENTRATION OF TARTARIC ACID IN AMMONIACAL SOLUTION.

(47)	1 g. TH_2 8 cc. NH_3..... in 100 cc.	48
(48)	2 g. TH_2 8 cc. NH_3..... in 100 cc.	95.5
(49)	3 g. TH_2 8 cc. NH_3..... in 100 cc.	145.5
(50)	4 g. TH_2 8 cc. NH_3..... in 100 cc.	193.5

EFFECT OF AMMONIA AND AMMONIUM CHLORIDE ON THE ROTATION OF CANE-SUGAR.

(51) 8.17 g. cane-sugar in 100 cc. 647
(52) 8.17 g. cane-sugar 8 cc. NH_3 in 100 cc. 641

THE SAME IN MORE DILUTE SOLUTION.

(55) 2 g. cane-sugar in 100 cc. 155
(56) 2 g. cane-sugar 4 cc. NH_3 in 100 cc. 155
(57) 2 g. cane-sugar 8 cc. NH_3 in 100 cc. 156
(58) 2 g. cane-sugar 16 cc. NH_3 in 100 cc. 161

Consequently more than 4 cc. free ammonia in 100 cc. should be avoided.

(59) 2 g. cane-sugar 4 cc. NH_3 8 g. ammonium chloride in 100 cc. 155

Note : 8 g. ammonium chloride are equivalent to about 16 cc. ammonia ; hence, the ammonium chloride has much less influence than the equivalent of ammonia.

EFFECT OF AMMONIA AND AMMONIUM CHLORIDE ON THE ROTATION OF INVERTED SUGAR.

A solution of 16.34 g. cane-sugar in 100 cc. was inverted according to Clerget's method, 50 cc. being heated with 5 cc. concentrated hydrochloric acid to 70° for ten minutes and made up to 100 cc. On adding ammonia, the solution turned gradually a bright yellow color, but during the change of color the reading did not appear to alter. (Temperature = 19°.)

(60) 20 cc. of the solution made up to 25 cc. 145.5
(61) 20 cc. of the solution 2 cc. NH_3 made up to 25 cc. 147.5
(62) 20 cc. of the solution 5 cc. NH_3 made up to 25 cc. 138

THE SAME IN MORE DILUTE SOLUTION. (Temperature = 18°.)

(63) Inverted sugar equivalent to 1.634 g. cane-sugar, 5 cc. concentrated hydrochloric acid in 100 cc 40
(64) Inverted sugar equivalent to 1.634 g. cane-sugar, 5 cc. concentrated hydrochloric acid, 8 cc. NH_3 40
(65) Inverted sugar equivalent to 1.634 g. cane-sugar, 5 cc. concentrated hydrochloric acid, 16 cc. NH_3 37
(66) Inverted sugar equivalent to 1.634 g. cane-sugar, 5 cc. concentrated hydrochloric acid, 6.8 cc. NH_3 39

Note : 5 cc. hydrochloric acid are equivalent to about 4 cc. ammonia so that these experiments show that a greater *excess* than 2 cc. in 100 cc. or 1 cc. in 50 cc. should be avoided.

EFFECT OF MAGNESIUM SULPHATE ON THE ROTATION OF SUGAR AND TARTARIC ACID.

(67) A solution was made up containing in 100 cc. the following :
14.4 g. sodium bicarbonate, 7.6 g. tartaric acid, 5 g. citric acid, and 4.2 g. sugar.
25 cc. of this solution, 2 cc. ammonia, 1.5 cc. concentrated hydrochloric acid made up to 50 cc 347

25 cc. of this solution, 2 cc. ammonia, 1 cc. hydrochloric acid, 5 g. magnesium sulphate made up to 50 cc 315

The same amount of magnesium sulphate, with ammonium chloride to prevent precipitation, has practically no effect on sugar alone.

EFFECT OF ALKALI AND ACID ON THE ROTATION OF TARTARIC ACID IN THE PRESENCE OF AMMONIUM MOLYBDATE.

(68)	3 g. TH_2 3.33 cc. NH_3	in 100 cc.	145
(69)	3 g. TH_2 45 cc. NH_3	in 100 cc.	147
(70)	3 g. TH_2 3.33 cc. NH_3, about 4 g. ammonium molybdate	in 100 cc.	1501
(71)	3 g. TH_2 45 cc. NH_3, about 4 g. ammonium molybdate	in 100 cc.	152
(72)	3 g. TH_2 3.33 cc. NH_3, about 4 g. ammonium molybdate, about 4 cc. concentrated nitric acid.....	in 100 cc.	1147
(73)	3 g. TH_2 3.33 cc. NH_3, about 4 g. ammonium molybdate, about 12 cc. concentrated nitric acid ...	in 100 cc.	445
(74)	0.64 g. KHT (impure), 0.65 cc. NH_3, 4 g. ammonium molybdate, 4 cc. normal acetic acid	in 100 cc.	297
(75)	0.64 g. KHT (impure), 0.65 cc. NH_3, 4 g. ammonium molybdate, 20 cc. normal acetic acid	in 100 cc.	337
(76)	0.64 g. KHT (impure), 0.65 cc. NH_3, 4 g. ammonium molybdate, 40 cc. normal acetic acid	in 100 cc.	355

THE NON-EFFECT OF ALUMINUM AND IRON SALTS, PHOSPHORIC ACID, AND SODIUM CARBONATE ON THE ROTATION OF TARTARIC ACID IN THE METHOD OF GROUP III.

In the following experiments the mixtures were treated according to the directions given under Group III.

(77)	0.1 g. KHT	65.5
(78)	0.1 g. KHT	66.5
(79)	0.1 g. KHT, 0.2 g. alum	65.5
(80)	0.1 g. KHT, 0.2 g. alum, 0.2 g. calcium acid phosphate.....	66.5
(81)	0.1 g. KHT, 0.1 g. sodium bicarbonate	66.5
(82)	Similar results were obtained using 0.2, 0.05, and 0.025 g. of KHT.	
(83)	0.2 g. KHT	130
(84)	0.2 g. KHT, 0.02 g. ferrous sulphate, 0.01 g. ferric chloride ..	130

The last two are earlier experiments and were made with solutions different from those described in the paper. For this reason the numbers are lower than those given below for 0.2 g. KHT, but the two readings show that iron has no influence.

EXPERIMENT TO TEST THE SOLUBILITY OF CALCIUM TARTRATE AND THE EFFECT OF STARCH.

The following were treated according to the method III.

(85)	0.2 g. KHT.....	134
(86)	0.1 g. KHT, 0.138 g. CaT (= 0.1 g. KHT), 0.2 g. alum, 0.3 g. phosphate cream of tartar substitute containing starch.....	133

THE ROTATION DUE TO INVERTED STARCH IN COMMERCIAL CREAM OF TARTAR SUBSTITUTES AND BAKING-POWDERS.

In the following experiments 8 g. of the sample and 8 cc. of concentrated ammonia were made up to 100 cc. (Note: Samples of corn starch, when treated in this way, gave filtrates which were practically inactive.)

	Description.	Brand.	Starch. Per cent.	Rotation.
(87)	Superphosphate substitute		26	8.3
(88)	Superphosphate substitute		13	10.4
(89)	Phosphate baking-powder	Q.	37	3.3
(90)	Alum baking-powder	H. C.	50	15.8
(91)	Alum baking-powder	J.	52	18.3
(92)	Alum-phosphate baking-powder	B. R.	48	2.9
(93)	Alum-phosphate baking-powder	W. S.	49	8.3
(94)	Alum-phosphate baking-powder	W. S.	49	11.0
(95)	Alum-phosphate baking-powder	W. S.	49	11.3
(96)	Alum-phosphate baking-powder	C.	46	0.2
(97)	Alum-phosphate baking-powder	G. S.	52	5.4
(98)	Alum-phosphate baking-powder	G. S.	52	5.6
(99)	Alum-phosphate baking-powder	W. E.	50	14.8
(100)	Alum-phosphate baking-powder	S. C.	51	10.4
(101)	Alum-phosphate baking-powder	U.	50	3.5

EXPERIMENTS TO SHOW THAT THE ROTATION OF INVERTED STARCH IS NOT INCREASED BY MOLYBDATE.

(102) 4 g. phosphate substitute, 8 cc. NH_3 to 100 cc 4

(103) 0.5 g. phosphate substitute, treated by molybdate method 0

(104) A solution of inverted starch was prepared by treating starch with sulphuric acid and removing the latter by barium carbonate. This solution was diluted so that:

20 cc. and 8 cc. NH_3 made up to 100 cc. gave 9

5 cc. of the same solution treated by molybdate method 2

RELATION BETWEEN AMOUNT OF TARTARIC ACID AND THE ROTATION IN THE MOLYBDATE METHOD.

The following are the averages of the best agreeing results of several experiments: In each case the substances were treated as described under III.

(105) 0.2 g. KHT 133

(106) 0.1 g. KHT 66

(107) 0.05 g. KHT 32

(108) 0.025 g. KHT 16.2

TEST ANALYSES BY THE SEVERAL METHODS DESCRIBED.

(109) *Test Analysis, Group I (1) and (2).*—Separation of cream of tartar and calcium tartrate. A mixture was made up of 2 g. KHT and 0.2 g. CaT and treated as directed under Group I (2) 167

The same mixture treated according to I (1) 157

The mixture contains 0.798 g. tartaric acid as bitartrate and 0.058 g. tartaric acid as calcium tartrate, or total $TH_2 = 0.856$ g.

The amounts calculated from the rotations are :

Total TH_2, 0.865 g., TH_2 as bitartrate, 0.815.

(110) *Test Analysis, Group II* (*1*).—A mixture was prepared corresponding to the sodii cit. tartras effervescens of the B.P.

13.72 grams sodium bicarbonate
4.92 grams citric acid
7.30 grams tartaric acid
4.06 grams sugar

30.00

The whole was dissolved in cold water and made up to 100 cc. (sol. *A*).

25 cc. of this solution and 1 cc. NH_3 made up to 50 cc. gave 334′ (*a*).

25 cc. of *A* required 4.2 cc. concentrated HCl to decolorize methyl violet.

25 cc. of *A* were heated with 4.2 + 2.5 cc. HCl to 70° for ten minutes, then methyl orange was added and 5 + 1 cc. NH_3. The solution, made up to 50 cc., gave a reading of..... (Temperature = 20°) 125′ (*b*) from which the sugar $z = 3.97$ g.

From this the rotation of the uninverted sugar in the 100 cc. is

$$3.97 \times 79.7 = 317',$$

and therefore the rotation of the tartaric acid

$$x = 2 \times 334 - 317 = 351,$$

from which the weight of tartaric acid

$$y = 4 \times 0.00519 \times 351 = 7.28.$$

(111) *Test Analysis, Group II* (*2*).—" Effervescing magnesium sulphate" (B.P.) was prepared as follows :

20.0 grams magnesium sulphate
14.4 grams sodium bicarbonate
7.6 grams tartaric acid
5.0 grams citric acid
4.2 grams sugar

The analysis was carried out exactly as described in the account of this method in the text, 3. g. sodium phosphate being used to precipitate the magnesium.

The following readings were obtained :

(*c*) 68′
(*d*) (Temperature = 18°) 13′

from which

$$\text{the sugar, } z = \frac{10 \times (68 - 2 \times 13) \times 1.254}{142 - \frac{1}{2}t} = 3.96,$$

and the tartaric acid,

$$y = 4\,(680 - 79 \times 3.96)\,0.00519 = 7.62.$$

In both the above experiments, it must be admitted, the tartaric acid comes out better than should be expected from the error in the sugar.

(112) *Test Analysis, Group III.*—The following mixture was made up and analyzed by the method described under the above head. 0.5 gram were taken for analysis.

1.0 gram potassium bitartrate
1.0 gram calcium tartrate
0.5 gram alum
1.0 gram phosphate tartar substitute

This mixture contains 32.9 per cent. tartaric acid.
Amount found: 33.4 per cent. tartaric acid.

UNIVERSITY OF MANITOBA,
UNIVERSITY OF TORONTO, } June, 1902.

[CONTRIBUTIONS FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE EQUIVALENT CONDUCTIVITY OF THE HYDROGEN ION DERIVED FROM TRANSFERENCE EXPERIMENTS WITH HYDROCHLORIC ACID.

BY A. A. NOYES AND G. V. SAMMET.

Received August 1, 1902.

I. PURPOSE OF THE INVESTIGATION.

IN calculating the degree of dissociation of a weak acid from its conductivity, it is first necessary to determine in some indirect way the value of its molar conductivity that corresponds to complete dissociation. This has been commonly done by adding to the molar conductivity of its sodium salt at extreme dilution the difference between that of hydrochloric acid and that of sodium chloride. The results so obtained may, however, be in error by a considerable amount, by reason of the fact that impurities in the water make it impossible to determine accurately the conductivity of hydrochloric acid (or any other strong acid) at a dilution where the dissociation is substantially complete. The values ordinarily employed have been obtained, therefore, by estimating, with the help of the change in the observed conductivity with the dilution, the probable effect of the impurities, and by making allowance for this effect.

A second, independent method that might be applied to the calculation of the molar conductivity of completely dissociated hydrochloric acid is to divide the equivalent conductivity of the chlorine ion by the transference number of moderately dilute hy-

drochloric acid. The former of these two values is already known with a fair degree of accuracy and certainty as a result of many transference and conductivity investigations on sodium and potassium chlorides. The latter has also been determined by Hittorf, Bein, Hopfgartner, and Jahn and Bogdan in connection with other transference experiments; but its importance in furnishing a reliable basis for the calculation of the dissociation-constants of acids has seemed to us to make it worthy of a more thorough investigation, especially as we had reason to expect that by employing the method previously described in this Journal[1] accurate results could be attained. It is the purpose of this article to present the results of such an investigation carried out with hydrochloric acid, mainly of 1/60 normal concentration and at the three temperatures of 10°, 20°, and 30°. To assist in the interpretation of the results, new determinations of the conductivity of the acid at these temperatures are also communicated.

II. PREPARATION AND STANDARDIZATION OF SOLUTIONS.

To insure their purity, all of the hydrochloric acid solutions submitted to electrolysis, except those numbered 1 and 2 for which chemically pure commercial acid was used, were made by diluting especially prepared concentrated solutions with water which had been distilled from alkaline permanganate. The concentrated acid used in the preparation of the solutions numbered 6, 7, 8, and 9 was made by generating hydrochloric acid gas by the action of pure concentrated sulphuric acid upon sodium chloride purified by previous precipitation with hydrochloric acid gas, conducting it through a wash-bottle containing a little water, and then absorbing it in pure water. For preparing solutions 3, 4, and 5, hydrochloric acid gas was generated by dropping concentrated sulphuric acid into pure concentrated hydrochloric acid solution; the gas was then washed and absorbed as before, and the resulting solution was appropriately diluted. The water used for all of the solutions employed in this investigation had at 25° a specific conductivity of less than 1.5×10^{-6} reciprocal ohms.

The hydrochloric acid solutions were standardized by precipitating 150-gram portions with silver nitrate with the addition of 2 cc. of strong nitric acid, heating half an hour to just below boil-

[1] Noyes: This Journal, 23, 39.

ing, collecting the precipitates, after washing them by decantation with cold water, in platinum Gooch crucibles, and drying them at 135° for twelve hours or more till the weight was constant to 0.1 milligram.

An approximately 0.1 normal barium hydroxide solution was prepared from the recrystallized commercial product, and was preserved in a bottle so arranged with a soda-lime tube and a delivery tube that portions could be drawn from it without introducing carbon dioxide from the air. It was proved to be entirely free from chloride by evaporating 100 cc. with nitric acid and testing with silver nitrate.

This barium hydroxide solution was standardized in terms of the hydrochloric acid solutions by titrating it with the help of phenolphthalein against 150-gram portions of the acid. Throughout these experiments all measurements of solutions were made by weight, and not by volume. The barium hydroxide solution was delivered from a long cylindrical 120-cc. drop-funnel, fitted with a perforated rubber stopper with a soda-lime tube, and having its delivery tube drawn to a point 10 cm. below the stop-cock. The drop funnel was filled by connecting the end of the delivery tube with the tube leading into the barium hydroxide bottle, and drawing the solution into the funnel by applying suction at the top, thus preventing the solution from coming into contact with the air. The end of the delivery tube was capped with a small test-tube during the weighings.

III. DESCRIPTION OF THE METHOD.

The apparatus used was that designed for the transference work previously done in this laboratory.[1] It consists of two large U-tubes of a bore of 3.5 cm. and a height of 40 cm., each of which has the top of one of its arms bent at right angles and has a small upright tube sealed into this bend so that the stem of a pipette can be introduced through it to the bottom of the U-tube. During the electrolysis the bent ends of the two tubes were joined by a piece of soft rubber tubing, and the tubes were clamped in a suitable support. The cathode was a spiral of platinum wire. The anode was a round plate of silver, 2 mm. thick, just large enough to enter the tube; it was riveted to a stout silver wire, which was

[1] Noyes: This Journal, 23, 42 (1901).

connected with a platinum wire sealed in a glass tube that passed through a rubber stopper fitting the mouth of the U-tube. The silver anode has, over the cadmium or zinc anode which has been hitherto employed, the advantage that no foreign substance is introduced by it into the solution, since only insoluble silver chloride is formed at its surface. This makes it possible to increase the proportion of the acid transferred.

Given in outline, the method of carrying out the transference experiments consisted in passing a suitable current for three hours through the standardized hydrochloric acid solutions in the apparatus just described, determining the quantity of electricity by means of silver voltameters placed in series with it, dividing the electrolyzed solution into a cathode, an anode, and three middle portions, titrating each of these except the anode portion with barium hydroxide to determine the concentration-changes of the hydrogen ion, and precipitating all five of them with silver nitrate and weighing the precipitates to determine the concentration-changes of the chlorine ion. From the analyses of the cathode and anode portions three separate values of the transference-number were obtained, and by the analysis of the middle portions it was made certain that no error arose through convection. In a few of the experiments, those first made, the acidimetric titrations were omitted, however.

The details of the procedure were as follows: Before filling the tubes with the solution each was weighed separately, the anode tube containing its electrode. They were then joined with a piece of tight-fitting soft rubber tubing, which was wired on and completely covered with vaseline to prevent danger of leakage. The anode tube was first filled with the acid solution up to 5 or 6 cm. of the top, and then corked tightly, the electrode being adjusted so as to be about 6 to 7 cm. below the surface of the liquid. The cathode tube was then charged with the solution until it half filled the outer arm; then the stopper with the electrode was tightly inserted, and the middle part of the apparatus completely filled through the small upright tubes, which were then stoppered. It was necessary to fill the anode tube to the higher level so as to lengthen that portion; for otherwise the changes in concentration would extend too far beyond the bend, up into the inner arm of the tube.

At least half an hour before the electrolysis was started, the U-tubes were immersed in a large thermostat at the proper temperature to such a depth that the middle horizontal part of the apparatus was entirely covered. When the temperatures had equalized themselves, the electrodes were connected through a switch, a 16-candle-power 220-volt lamp, a Weston milliammeter, and two silver voltameters, with the terminals of a 110-volt circuit; and the current was turned on. The silver voltameters consisted of platinum dishes (which served as the cathodes) containing a 15 per cent. silver nitrate solution, just beneath the surface of which was placed a horizontal silver plate (to serve as anode) which was wrapped with filter-paper, and supported by a silver rod riveted through it. One of these voltameters was inserted at each end of the electrolytic apparatus. The milliammeter served only to indicate roughly the strength of the current.

The electrolysis was allowed to continue for three hours in all the experiments. The current was closely watched, and, if at any time it tended to diminish, the external resistance was changed, so as to keep the current approximately constant.

At the end of the electrolysis, the cathode was removed, shaking off any drops that adhered to it, and a rubber stopper was inserted in its place. The stoppers in the middle upright tubes were then removed, and three middle portions were withdrawn slowly by means of a pipette connected with a suction pump, the tip being lowered gradually so as to be always just beneath the surface of the liquid. These portions were transferred to tared flasks and weighed. The first portion extended to just below the bend in the middle horizontal part of the tubes; the other two portions reached in the inner arms to just above the level of the bends at the bottom of the tubes. The apparatus was next removed from the thermostat and separated at the rubber band; the tubes were wiped dry on the outside; the liquid adhering to the inside of the upper part of the middle arms was also removed; and the tubes were then weighed separately.

The cathode portion was now titrated in the tube by adding barium hydroxide solution from a weighed drop-funnel such as was described in Section 2 above. It was then transferred to a beaker and analyzed for its chlorine-content in the same manner as the solution had been previously standardized. The middle por-

tions, also, were titrated with the alkali, and then analyzed for chlorine in the same way. The anode portion when titrated with barium hydroxide was found to give utterly discordant results, owing probably to the liberation of some oxygen at the electrode and the production of a corresponding quantity of acid. It was therefore not titrated in most of the experiments. Its chlorine-content was determined in the following manner. The main solution containing silver chloride in suspension was poured into a beaker from the U-tube, which was rinsed out with enough ammonia to dissolve all the precipitate. The electrode, which was incrusted with silver chloride, was treated for an hour with concentrated ammonia with frequent rubbing; and after decanting the solution into the main solution, the electrode and the deposit of loose silver from it were warmed with nitric acid, until the surface layer had dissolved off the electrode. The solution and any residue of silver chloride remaining were washed into the main solution, which had meanwhile been filtered to remove particles of silver. The solution was now made acid with nitric acid and treated with an excess of silver nitrate, the precipitate being collected and weighed as before.

The filtrate from the silver chloride precipitate was treated with sulphurous acid and allowed to stand on a hot plate over night, in order to test it for free chlorine or oxyacids of chlorine. In only one of the final determinations did a precipitate appear; this was filtered off, washed and weighed, and added to the main quantity of the silver chloride precipitated. In several preliminary determinations, however, it was found that the anode values were abnormally low, and that the filtrate from the silver chloride gave a considerable precipitate with sulphurous acid on standing ten to twelve hours. This difficulty was entirely removed by reducing the current density. It was found that when the current was less than 4.5 milliamperes per square centimeter no free chlorine was generated.

After the electrolysis had continued for an hour or so, it was occasionally observed that the current rapidly decreased, owing to an increase in the resistance at or near the anode. This arose either from its becoming too thickly coated with silver chloride or from the solution in its immediate neighborhood becoming nearly exhausted. The first of these effects was greatly diminished by

reducing the current-strength; the second, by placing the anode 6 to 8 cm. below the surface of the liquid, so that the weakened solution would rise and cause a slow stirring in the neighborhood of the electrode, thus increasing the quantity of electrolyte available for electrolysis. Under these conditions, the current could be kept practically constant during the three hours of an experiment.

In every experiment, the silver chloride formed a cloud around the anode and then extended slowly down the tube to the bend, where it formed a perfectly sharp line at the level of the top of the bend. The formation and maintenance of this sharp line showed conclusively that there was no stirring taking place in the tubes.

IV. THE EXPERIMENTAL DATA AND RESULTS.

The first experiments were made with approximately 1/20 normal hydrochloric acid; but most of the work was done upon an acid three times more dilute, as this was about the limit to which the dilution could be carried without some sacrifice of experimental accuracy. The exact concentrations of the various solutions employed are given in the following table expressed in milligrams of silver chloride per gram of solution. Each value is the mean derived from a series of analyses, and its probable accuracy is indicated by the number of these and its average deviation (A. D.).[1]

Solution number.	Analyses made.	Concentration.	A. D. of the result.
1	3	7.3651	0.0001
2	3	7.7091	0.0007
3	3	6.7519	0.0013
4	3	7.3924	0.0017
5	3	2.4813	0.0011
6	3	2.4537	0.0007
7	4	2.5268	0.0008
8	5	2.4718	0.0003
9	4	2.4789	0.0001

Two different barium hydroxide solutions were employed. The first of these, approximately 1/6 normal, was standardized separately against acid solution No. 7 and another standard hydrochloric acid solution which was not used in the final experiments, and its concentration was found to correspond to 24.203 and

[1] This is the average deviation (a. d.) of the separate values from the mean divided by the square root of the number of values and is equal to 1.18 times the "probable error."

24.191 milligrams silver chloride per gram solution, respectively, the divergence being therefore only 0.05 per cent. The second solution, roughly 1/12 normal, was standardized against solutions Nos. 8 and 9, and its concentration was found to correspond to 12.612 and 12.600 milligrams silver chloride per gram solution, respectively (divergence, 0.1 per cent.). Each barium hydroxide solution was used in titrating, after the electrolysis, the acid solutions against which it had been standardized.

The data of the experiments and the calculated transference values are given in the following tables. The *first* column contains the number of the experiment; the *second*, the number of the acid solution used; the *third*, letters representing the different portions submitted to analysis, K signifying the cathode solution, M_K the adjoining middle portion, M the next portion, M_A the portion adjoining the anode, and A the anode portion itself; the *fourth* gives the weight in grams of the portions analyzed; the *fifth* column, vacant in the case of the first fourteen experiments, contains the number of grams of barium hydroxide solution used in neutralizing the portions after the electrolysis; the *sixth* contains the initial content expressed in milligrams of silver chloride as calculated from the weight of the portion and the standardization value; the *seventh*, the final content determined by direct weighing of the silver chloride, and, on the line below, except in the first fourteen experiments, the value of it calculated from the barium hydroxide used; the *eighth*, the change in content of the separate portions; the *ninth*, the total change in content, which includes the changes in the portions adjoining the cathode and anode; the *tenth*, the milligrams of silver precipitated in the voltameters; and the *eleventh*, the calculated transference numbers multiplied by 1000.[1]

[1] The way in which these were calculated may be illustrated with the help of the data obtained in the second experiment. The cathode portion submitted to analysis weighed 452.76 grams and was found to yield 3158.8 mg. of silver chloride. To determine the original content the weight of the portion is multiplied by the original concentration of the solution (7.3651 mg.), which gives 3334.6. The decrease in concentration at the cathode is, therefore, 175.8 mg. Adding to this the decrease in the adjoining middle portion (1.0 mg.) and dividing by the equivalent weight of silver chloride (143.38) and by the number of equivalents of silver (803.3/107.93) precipitated in the voltameter, the transference number is found to be 0.1656.

$^1/_{25}$-MOLAR HCl AT 20°.

Expt. No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference numbers.
1	2	3	4	5	6	7	8	9	10	11
1	1	K	454.42		3346.9	3177.1	—169.8	—169.8		164.9
		M_K	142.03		1046.1	1046.2	+ 0.1			
		M	191.04		1407.0	1407.2	+ 0.2		775.8	
		M_A	125.84		926.9	924.7	— 2.2			
		A	460.88		3394.5	3566.2	+171.7	+169.5		164.2
2	1	K	452.76		3334.6	3158.8	—175.8	—176.8		165.6
		M_K	147.35		1085.3	1084.3	— 1.0			
		M	177.29		1305.2	1304.9	— 0.3		803.3	
		M_A	137.06		1009.5	1006.3	— 3.2			
		A	468.79		3452.8	3631.2	+178.4	+175.2		164.2
3	1	K	450.38		3317.0	3150.8	—166.2	—166.7		165.9
		M_K	140.93		1038.0	1037.5	— 0.5			
		M	182.69		1345.5	1345.3	— 0.2		756.6	
		M_A	138.10		1017.1	1015.5	— 1.6			
		A	474.20		3492.5	3662.9	+170.4	+168.8		167.9
4	1	K	446.61		3289.4	3110.4	—179.0	—179.5		166.3
		M_K	145.20		1069.4	1068.9	— 0.5		812.6	
		M	181.60		1337.5	1337.8	+ 0.3		813.6	
		M_A	121.14		892.2	891.2	— 1.0			
		A	474.65		3496.0	3677.0	+181.0	+180.0		166.6
5	2	K	445.78		3436.5	3258.6	—177.9	—178.6		164.2
		M_K	149.21		1150.3	1149.6	— 0.7		819.6	
		M	177.17		1365.8	1365.0	— 1.8		817.4	
		M_A	136.20		1050.0	1044.3	— 5.7			...
		A	462.44		3565.0	3750.0	+185.0	+179.3		164.9
6	3	K	465.79		3144.2	2987.6	—156.6	—157.8		164.9
		M_K	131.02		884.4	883.2	— 1.2		718.6	
		M	153.42		1035.6	1035.3	— 0.3		718.6	
		M_A	141.65		956.1	950.8	— 5.3			
		A	479.02		3233.5	3395.5	+162.0	+156.7		164.2
7	4	K	472.52		3493.0	3333.0	—160.0	—160.0		165.3
		M_K	125.31		926.3	926.4	+ 0.1		729.1	
		M	192.57		1423.4	1422.5	— 0.9		728.0	...
		M_A	125.44		927.3	921.2	— 6.1			
		A	469.99		3473.3	3640.2	+166.9	+160.8		166.1

Expt. No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameter.	Transference number.
1	2	3	4	5	6	7	8	9	10	11
8	4	K	470.45		3477.8	3314.0	—163.8	—163.8		166.8
		M_K	136.10		1006.0	1005.9	— 0.1			
		M	183.20		1354.1	1353.7	— 0.4		739.0	
		M_A	132.97		983.0	978.8	— 4.2		739.2	
		A	457.91		3385.0	3551.3	+167.3	+163.1		166.1
9	4	K	425.61		3146.2	2999.3	—146.9	—146.9		168.7
		M_K	142.24		1051.5	1051.5	± 0.0			
		M	168.96		1249.0	1248.5	— 0.5		656.1	
		M_A	136.19		1006.8	1002.2	— 4.6		655.8	
		A	444.08		3282.8	3431.5	+148.7	+144.1		165.4
					$^1/_{60}$-MOLAR HCl AT 20°.					
10	5	K	355.76		882.7	811.8	— 70.9	— 70.9		167.3
		M_K	96.06		238.3	238.3	± 0.0			
		M	138.42		334.4	334.0	— 0.4		318.7	
		M_A	128.67		319.1	318.0	— 1.4		319.1	
		A	455.08		1129.2	1201.1	+ 71.9	+ 70.5	...	166.2
11	5	K	363.86		902.8	837.8	— 65.0	— 65.0		169.0
		M_K	96.28		238.8	238.7	— 0.1			
		M	172.85		428.9	427.6	— 1.3		289.2	
		M_A	113.91		282.6	282.0	— 0.6		289.3	
		A	462.17		1146.7	1211.1	+ 65.6	+ 65.0		169.0
12	6	K	470.13		1154.0	1105.8	— 48.2	— 48.2		165.3
		M_K	139.06		341.3	341.6	+ 0.3			
		M	198.19		486.5	486.6	+ 0.1		219.6	
		M_A	150.33		369.0	367.9	— 1.1		219.5	
		A	441.61		1084.0	1034.3	+ 49.7	+ 48.6		166.7
13	6	K	361.54		887.5	839.6	— 47.9	— 47.9		164.1
		M_K	94.13		231.0	231.3	+ 0.3			
		M	147.26		361.5	361.6	+ 0.1		219.5	
		M_A	187.43		460.2	460.3	+ 0.1		219.6	
		A	420.39		1031.8	1080.7	+ 48.9	+ 48.9		167.9
14	6	K	483.59		1186.7	1123.1	— 63.6	— 63.6		166.3
		M_K	143.17		351.4	351.3	+ 0.1			
		M	216.48		531.3	531.2	— 0.1		287.4	
		M_A	106.86		262.3	261.1	— 1.2		287.7	
		A	466.11		1143.8	1209.3	+ 65.5	+ 64.3		168.2

Expt. No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference numbers.
1	2	3	4	5	6	7	8	9	10	11
15	7	K	332.94		841.2	764.5	— 76.7	— 76.7		166.9
				31.59		764.3	— 76.9	— 77.4		168.3
		M_K	201.41		509.0	509.1	+ 0.1			
				21.02		508.5	— 0.5		346.1	
		M	193.79		489.7	489.7	± 0.0		345.9	
				20.23		489.5	— 0.2			
		M_A	179.29		453.1	452.3	— 0.8			
				18.68		452.1	— 1.0			
		A	372.48		941.2	1015.3	+ 74.1	+ 73.3		159.3
16	7	K	341.83		863.8	787.0	— 76.8	— 76.6		166.4
				32.52		786.6	— 77.2	— 77.0		167.2
		M_K	196.70		497.0	497.2	+ 0.2			
				20.55		497.2	+ 0.2			
		M	172.22		435.2	434.2	— 1.0		346.5	
				17.95		434.5	— 0.7		346.7	
		M_A	190.13		480.4	478.9	— 1.5			
				19.76		478.0	— 2.4			
		A	374.58		946.5	1024.0	+ 77.5	+ 76.0		165.4
17	8	K	332.90		822.8	744.6	— 78.2	— 77.7		167.3
				59.05		744.8	— 78.0	— 78.3		168.5
		M_K	197.43		488.0	488.5	+ 0.5			
				38.67		487.7	— 0.3		349.7	
		M	193.65		478.6	478 0	— 0.6		349.5	
				37.91		478.1	— 0.5			
		M_A	174.96		432.4	430.6	— 1.8			
				34.10		430.0	— 2.4			
		A	360.70		891.6	970.8[1]	+ 79.2	+ 77.4		166.7
18	8	K	323.45		799.4	730.2	— 69.2	— 69.2		166.7
				57.90		730.2	— 69.2	— 69.5		167.4
		M_K	193.69		478.7	478.8	+ 0.1			
				37.94		478.4	— 0.3		312.4	
		M	182.17		450.3	450.1	— 0.2		312.2	
				35.71		450.4	+ 0.1			
		M_A	179.51		443.7	442.1	— 1.6			
				35.03		441.7	— 2.0			
		A	390.81		965.9	1037.0	+ 71.1	+ 69.5		167.4

[1] In the analysis of this portion some silver chloride was obtained on boiling the filtrate from the silver nitrate precipitate, with sulphurous acid. This silver chloride was filtered, washed, weighed, and added to the weight of the first silver chloride precipitate. It amounted to 3.4 mg.

Expt. No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference numbers.
1	2	3	4	5	6	7	8	9	10	11
19	9	K	313.08		776.2	701.5	— 74.7	— 74.7		166.8
				55.66		701.2	— 75.0	— 75.0		167.5
		M_K	185.94		460.9	461.0	+ 0.1			
				36.60		461.0	+ 0.1		337.2	
		M	206.43		511.8	511.8	± 0.0		337.1	
				40.61		511.7	— 0.1			
		M_A	181.86		450.9	449.4	— 1.5			
				35.69		449.6	— 1.3			
		A	415.00		1028.8	1104.0	+ 75.2	+ 74.7		166.8
20	9	K	315.55		782.3	704.9	— 77.4	— 77.2		168.2
				55.97		705.1	— 77.2	— 77.2		168.2
		M_K	188.97		468.5	468.7	+ 0.2			
				36.42		468.6	+ 0.1		346.0	
		M	202.38		501.7	501.6	— 0.1		345.9	
				39.81		501.6	— 0.1			
		M_A	185.19		459.1	459.1	± 0.0			
				36.42		459.2	+ 0.1			
		A	410.17		1016.9	1093.8	+ 76.9	+ 76.9		167.3
					* $1/_{60}$-MOLAR HCl AT 10°.					
21	8	K	309.08		764.0	693.9	— 70.1	— 69.8		158.3
				lost						
		M_K	197.73		488.7	489.0	+ 0.3			
				38.76		488.8	+ 0.1		331.9	
		M	184.62		456.3	456.1	— 0.2		331.8	
				36.17		456.2	— 0.1			
		M_A	191.34		473.0	473.4	+ 0.4			
				37.50		473.4	± 0.0			
		A	409.12		1011.3	1080.2	+ 68.9	+ 69.3		157.1
22	8	K	333.89		825.3	755.9	— 69.4	— 69.4		158.9
				59.98		756.5	— 68.8	— 68.9		157.8
		M_K	193.83		479.1	479.1	± 0.0			
				37.98		479.0	— 0.1		328.8	
		M	150.23		371.3	371.3	± 0.0		328.6	
				29.44		371.3	± 0.0			
		M_A	196.16		484.9	484.9	± 0.0			
				38.44		484.9	± 0.0			
		A	426.77		1054.9	1124.4	+ 69.5	+ 69.5		159.1

Expt. No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference numbers.
1	2	3	4	5	6	7	8	9	10	11
23	8	K	321.79		795.3	726.8	— 68.5	— 68.5		158.8
				57.66		727.2	— 68.1	— 68.4		158.6
		M_K	195.70		483.7	483.8	+ 0.1			
				38.42		483.4	— 0.3		324.7	
		M	167.45		413.9	413.8	— 0.1		324.7	
				32.82		413.8	— 0.1			
		M_A	194.57		480.9	480.8	— 0.1			
				38.11		480.6	+ 0.3			
		A	406.20		1004.2	1073.0	+ 68.8	+ 68.8		159.4
24	9	K	305.05		756.2	689.6	— 66.6	— 66.6		159.2
				54.74		689.6	— 66.6	— 66.6		159.2
		M_K	184.30		456.9	456.8	— 0.1			
				36.25		456.8	— 0.1		315.1	
		M	194.00		480.9	480.6	— 0.3		315.0	
				38.16		480.8	— 0.1			
		M_A	176.45		437.4	437.1	— 0.3			
				34.70		437.1	— 0.3			
		A	405.62		1005.6	1072.0	+ 66.4	+ 66.1		158.0
25	9	K	307.11		761.4	693.6	— 67.8	— 67.8		157.4
				55.04		693.3	— 68.1	— 68.1		158.0
		M_K	192.27		476.6	476.5	— 0.1			
				37.83		476.6	± 0.0		324.4	
		M	199.80		495.3	495.4	+ 0.1		324.2	
				39.31		495.2	— 0.1			
		M_A	186.63		462.7	462.7	± 0.0			
				36.71		462.6	— 0.1			
		A	407.20		1609.5	1073.0	+ 63.5	+ 63.5	...	147.4
26	9	K	311.78		773.0	707.7	— 65.3	— 65.3		159.6
				56.26		708.7	— 64.3	— 64.3		157.1
		M_K	187.16		464.0	464.1	+ 0.1			
				36.84		464.1	+ 0.1		307.9	
		M	192.71		477.7	477.8	+ 0.1		308.0	
				37.93		477.8	+ 0.1			
		M_A	196.10		486.1	486.0	— 0.1			
				38.58		486.0	— 0.1		...	
		A	410.84	...	1018.5	1083.5	+ 65.0	+ 65.0		158.9

$^1/_{60}$-MOLAR HCl AT 30°.

Expt. No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference numbers.
1	2	3	4	5	6	7	8	9	10	11
27	7	K	321.75		813.2	730.3	— 82.9	— 84.4		176.1
				30.18		729.9	— 83.3	— 84.8		176.8
		M_K	186.21		470.6	469.1	— 1.5			
				19.39		469.1	— 1.5		361.3	
		M	152.06		384.2	384.1	— 0.1		361.4	
				15.84		383.3	— 0.9			
		M_A	206.28		521.2	518.6	— 2.6			
				21.41		518.1	- 3.1			
		A	384.70		972.1	1059.8	+ 87.7	+ 85.1		177.4
28	7	K	308.08		778.5	701.0	— 77.5	— 78.7		177.6
				28.99		701.3	— 77.2	— 78.4		176.9
		M_K	198.08		500.5	499.3	— 1.2			
				20.64		499.3	— 1.2		333.4	
		M	178.00		449.7	449.4	— 0.3		333.6	
				18.58		449.5	— 0.2			
		M_A	195.76		494.7	492.7	— 2.0			
				20.38		493.0	— 1.7			
		A	388.75		982.3	1063.1	+ 80.8	+ 78.8		177.9
29	7	K	314.65		795.1	741.1	— 54.0	— 54.1		177.3
				30.64		741.1	— 54.0	— 54.0		177.0
		M_K	200.42		506.4	506.3	— 0.1			
				20.94		506.4	± 0.0		229.5	
		M	166.17		420.0	420.1	+ 0.1		229.8	
				17.36		420.0	± 0.0			
		M_A	214.62		542.4	542.2	— 0.2			
				22.42		541.9	— 0.5			
		A	369.04		932.5	987.0	+ 54.5	+ 54.3		177.9
30	7	K	313.30		791.7	709.6	— 82.1	— 83.5		177.5
				29.34		709.7	— 82.0	— 83.4		177.3
		M_K	193.66		489.3	487.9	— 1.4			
				20.17		487.9	— 1.4		354.0	
		M	163.43		413.0	412.9	— 0.1		354.1	
				17.03		412.3	— 0.7			
		M_A	185.48		468.7	467.4	— 1.3			
				19.31		467.0	— 1.7			
		A	397.80		1005.3	1090.3	+ 85.0	+ 83.7		177.9

Expt. No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference numbers.
1	2	3	4	5	6	7	8	9	10	11
31	7	K	325.45		822.4	753.0	— 69.4	— 67.6		165.9
				31.08		751.7	— 70.7	— 72.2		177.2
		M_K	197.36		498.8	499.6	+ 0.8			
				20.56		497.3	— 1.5		306.5	
		M	200.17		505.8	505.8	± 0.0		306.8	
				20.90		505.3	— 0.5			
		M_A	188.13		475.4	474.0	— 1.4			
				19.60		473.7	— 1.7			
		A	367.01		927.4	1001.3	+ 73.9	+ 72.5		177.9
32	7	K	336.86		851.3	764.7	— 86.6	— 87.8		177.3
				31.61		764.7	— 86.6	— 87.6		176.9
		M_K	190.35		481.0	479.8	— 1.2			
				19.84		480.0	— 1.0		372.7	
		M	196.66		496.9	496.6	— 0.3		372.8	
				20.54		496.2	— 0.7			
		M_A	181.63		459.0	458.5	— 0.5			
				18.90		457.3	— 1.7			
		A	364.89		922.0	1009.8	+ 87.8	+ 87.3		176.3

V. SUMMARY OF THE TRANSFERENCE VALUES.

All the values of the transference numbers derived from the experiments recorded are summarized in the following tables:

$^1/_{20}$-MOLAR HCl AT 20°.

Expt. No.	Anode.	Cathode.
1	164.2	164.9
2	164.2	165.6
3	167.9	165.9
4	166.0	165.3
5	164.9	164.2
6	164.2	164.9
7	166.1	165.3
8	166.1	166.8
9	165.4	168.7
Mean,	165.51	165.84
a.d.,	1.03	0.96
A.D.,	0.34	0.32
Final mean,		165.69
A.D.,		0.12

$^1/_{60}$-MOLAR HCl AT 20°.

Expt. No.	Anode.	Cathode from AgCl.	Cathode from BaO_2H_2.
10	166.2	167.3	
11	169.0	169.0	
12	166.7	165.3	
13	167.9	164.1*	
14	168.2	166.3	
15	159.3*	166.9	168.3
16	165.4	166.4	167.2
17	166.7	167.3	168.5
18	167.4	166.7	167.4
19	166.8	166.8	167.5
20	167.3	168.2	168.2
Mean,	167.16	167.02	167.85
a.d.,	0.80	0.74	0.48
A.D.,	0.25	0.23	0.19
Final mean,		167.43	
A.D.,		0.25	

$^1/_{80}$-MOLAR HCl AT 10°.

Expt. No.	Anode.	Cathode from AgCl.	Cathode from BaO_2H_2
21	157.1*	158.3	lost
22	159.1	158.9	157.8
23	159.4	158.8	158.6
24	158.0	159.2	159.2
25	147.4*	157.4	158.0
26	158.9	159.6	157.1
Mean,	158.85	158.70	158.14
a.d.,	0.42	0.57	0.61
A.D.,	0.21	0.23	0.27

Final mean, 158.62
A.D., 0.15

$^1/_{80}$-MOLAR HCl AT 30°.

Expt. No.	Anode.	Cathode from AgCl.	Cathode from BaO_2H_2.
27	177.4	176.1*	176.8
28	177.9	177.6	176.9
29	177.9	177.3	177.0
30	177.9	177.5	177.3
31	177.9	165.9*	177.2
32	176.3*	177.3	176.9
Mean,	177.80	177.42	177.01
a.d.,	0.16	0.12	0.15
A.D.,	0.08	0.06	0.06

Final mean, 177.34
A.D., 0.16

In obtaining the means of the values by each different method, those values designated by an asterisk in the tables were omitted. These values all deviate from the mean calculated without them by more than four times the average deviation of the other values from the mean. This average deviation is represented in the tables by a.d. By dividing this by the square-root of the number of observations, the "average deviation of the mean" represented by A.D. was calculated. The "final means" were obtained by combining the separate means, assigning to each a weight inversely proportional to the square of its A.D.

VI. PROBABLE ACCURACY OF THE RESULTS.

The probable degree of accuracy of the results both with respect to accidental and systematic errors may first be considered. In this connection it should be stated that all the determinations are recorded which were carried to completion after the method was perfected.

The four things that might affect the accuracy of the results are impurities in the acid solution electrolyzed, inaccuracy or variation in the temperature, errors in the voltameter measurements, and errors in the electrolysis or analysis of the solutions.

The purity of the samples of acid used is perhaps sufficiently demonstrated by their methods of preparation, and that of the water by its slight conductivity. That the acid solutions contained no impurity that could affect the results is further proved by the agreement of the transference values obtained with the acid from

three different sources,[1] of the electrical conductivity (in the case of solution 9) with that found by other investigators (see below), and of the transference numbers calculated from the H' concentrations with those calculated from the Cl' concentrations, thus proving that no other ions participated in the transference.

The temperatures were determined with a thermometer which was corrected by comparison with the standard of the Physical Department of this Institute. They were kept constant during the experiments within 0.02°, which is entirely sufficient as the temperature-coefficient of the transference-number is 0.6 per cent. per degree.

The voltameter measurements were made in accordance with the legal specifications, and were checked in almost all the experiments by inserting in the circuit two voltameters, one on each side of the electrolysis apparatus, thus preventing any error from leakage of electricity. The two values will be seen to check within 0.1 per cent. in all cases.[2]

Of the errors in the electrolysis and analysis of the solution the results themselves furnish a criterion in four different ways: namely, through a consideration of (1) the changes in concentration of the middle portions; (2) the agreement of the similarly determined transference-numbers in the different experiments; (3) the agreement of those calculated from concentration-changes at the two different electrodes in the same experiment; and (4) the agreement of those calculated from the concentration-changes of the two different ions. These four considerations will be taken up in the order named.

(1) It will be seen that the change in the middle portion of all is in only a very few cases more than 0.05 per cent and therefore no greater than the analytical error, and that the changes in the two adjoining middle portions are very small, showing that the changes at the electrodes were caused only by the transference and were

[1] Thus experiments 1–5 were made with solutions prepared from chemically-pure commercial acid, experiments 12–32 with solutions made from hydrochloric acid gas generated from sodium chloride, and experiments 6–11 with solutions made from hydrochloric acid gas liberated from the commercial acid.

[2] We have not thought it necessary to correct our results for the deviation shown to exist by Richards, Collins, and Heimrod (*Proc. Am. Acad.*, 35, 123) between the results of the legal silver voltameter and the requirements of Faraday's law; for this deviation amounts to less than 0.1 per cent.

not at all affected by convection currents. That there was no convection on the anode side was also shown, as was stated above, by the sharp line formed by the finely suspended silver chloride in the bend of the tube. No error was possible, of course, from the participation in the transference of foreign ions produced by the electrolysis; for the materials of the electrodes precluded this.

(2) The percentage average deviations (100 a.d./mean) of the separate values from the mean are nearly identical for the gravimetric cathode and anode values in each of the four series of experiments, and amount to 0.59, 0.44, 0.13, 0.09 with 1/20 molar HCl at 20°, and 1/60 molar at 20°, at 10°, and at 30°, respectively. The corresponding percentage "average deviations of the mean" (100 A.D./mean) are 0.19, 0.14, 0.14 and 0.04, respectively. These last values may be regarded as measures of the precision of the separate means, as far as the effect of accidental errors is concerned.

(3) It will be seen from the summary of the transference-values that the means calculated from the anode-portion analyses do not differ from those from the cathode-portion analyses by more than 1/4 per cent. in any one of the four series of experiments. Moreover, the average deviations of these means are nearly identical, thus showing that the more complicated procedure in the case of the anode portion did not introduce any error. This agreement not only eliminates to a greater extent the effect of accidental errors, but proves the absence of certain imaginable systematic errors of a greater magnitude than this, in the analysis of the solution; for, since at the cathode there is a decrease and at the anode an increase in the chlorine-content, the results would be affected by such errors in opposite directions; thus, this is true of errors in the determination of the original-content of the solution and of errors from loss of silver chloride or particles of asbestos from the crucibles in the final analyses.

(4) The mean transference-numbers calculated from the acidimetric titrations differ from those derived from the silver-chloride weighings by 0.33-0.39 per cent. in the three different cases. Within these limits, therefore, the agreement of the results by the two independent methods of analysis gives a further confirmation

of the accuracy of the analytical work. It shows, also, as stated above, that no ions other than those coming from the hydrochloric acid took part in the transference.

As the final means were obtained by a combination of the results of the three series of independent analyses, and as it is not possible that there was any considerable error except in connection with the electrolyzed solution, the average deviations of the final means are a measure of their probable accuracy with respect to errors from all sources. These average deviations lie between 0.10 and 0.15 per cent. in the case of the four series of experiments. It seems certain that the actual error cannot in any case exceed three times the larger of these deviations or 0.45 per cent. The probable and possible percentage errors would, of course, be only about one-fifth as great if the results were calculated for the cathion (instead of for the anion), as has been done by some investigators.

VII. COMPARISON WITH THE RESULTS OF PREVIOUS INVESTIGATIONS.

Transference numbers for hydrochloric acid were first published by Hittorf in his original memoirs on the general subject. As the values in the dilute solutions deviate greatly from all those more recently obtained, and as their accuracy was doubted by that investigator himself, they do not need to be considered here. Within the last four years, however, three other series of determinations have been communicated, namely by Hopfgartner,[1] Bein,[2] and Jahn and Bogdan.[3] We have reduced their determinations, which were made between 9° and 19°, to 20° by means of the temperature-coefficient which we found between 10° and 20°, which is identical, moreover, with that given by Bein. We recall that our values at 20° are 165.69 (A.D. = 0.12, 9 experiments, 18 values) for the 1/20 molar solution, and 167.43 (A.D. = 0.25, 11 experiments, 26 values) for the 1/60 molar solution. Hopfgartner's results with 1/10 and 1/5 molar solutions lead to 168.0 (A.D. = 1.6; 9 values); Bein's with 1/7 to 1/70 molar, to 172.4

[1] *Ztschr. phys. Chem.*, **28**, 135 (1898).
[2] *Ibid.*, **27**, 32, 49 (1898).
[3] *Ibid.*, **37**, 679 (1901).

(A.D. = 1.7; 5 values[1]; Jahn and Bogdan's, with 1/32 to 1/80 molar, to 176.0 (A.D. = 0.85; 11 values).

In view of the large average deviations of these results, their wide divergence from one another, and the facts that, except in the case of Bein's, they were not controlled by analyses of the portions at both electrodes and that in the cases of all of them the middle portions exhibited considerable changes, it seems probable that our values are nearer the true ones than any that might be obtained by combining them with these earlier results. The greater errors in these probably arose from two causes: first, the changes in concentrations in the portions around the electrode were small, amounting only to from 2 to 6 per cent. of the total salt-content; and secondly, a considerable proportion of the changes in concentration that did occur was in the middle portion, this proportion amounting to from 3 to 8 per cent. in most of Bein's experiments; in Jahn and Bogdan's experiments the percentage changes in concentration indicate that it was considerable, but the proportion of the total change cannot be stated since they failed to give the weights of the middle portion. In our experiments the changes in concentration were from 10-15 per cent. of the total salt content, and the changes in the middle portions were only from 0.1 to 0.3 per cent. of the total change.

VIII. CHANGE OF THE TRANSFERENCE-NUMBERS WITH THE CONCENTRATION.

It will be seen that at 20° the transference-number increases by just about 1 per cent. in passing from the dilution of 20 to that of 60 liters. It is not impossible that this apparent change arises wholly from experimental errors, as the 1/20 molar solution was the one first investigated, the average deviation of the separate values from the mean is greater than in any other case, and the results were not checked by an acidimetric titration. Still it is not probable that this is the case; for it would be necessary to assume errors of about three times the A.D's in the final means of both the 1/20 and 1/60 molar solutions, and that these lay in opposite directions. Even assuming that the whole change is real, it is still small enough to indicate that the value at infinite dilution cannot differ much from that at 1/60 molar. This is made still

[1] The two experiments to which a weight of ½ is assigned are here considered as one. The three to which a weight of ¼ is given are left entirely out of consideration.

more probable by the consideration that the undissociated portion of the acid at that dilution amounts to only 6 per cent., and especially by the results of Jahn and Bogdan, which show no systematic change whatever in the transference-number between the dilutions of 32 and 110 liters. Still it must be admitted, that, though not probable, yet it is possible that an error of 1 to 2 per cent. would be made by assuming no further change in the transference number after 1/60 molar is reached.

IX. MEASUREMENTS OF THE CONDUCTIVITY OF HYDROCHLORIC ACID.

To assist in the discussion of the results it was desirable to know the temperature-coefficient of the conductivity of the hydrochloric acid between the temperatures in question. The conductivity of the acid was therefore measured by the usual Kohlrausch method at 10°, 20°, and 30° and at two dilutions. The results are given in the following table. The first column gives the temperature; the second, the volume in true liters[1] containing 1 mol; the third, the measured conductance in reciprocal ohms; the fourth, the molar conductivity calculated therefrom[2], and referred to the cubic centimeter as the unit of volume; the fifth, the values of it calculated from Kohlrausch's data[3] at 18° and Déguisne's temperature-coefficients[4]; and the sixth, the changes in conductivity for each interval of 10°.

Temperature.	Dilution.	Conductance.	Molar conductivity. N. and S.	Molar conductivity. K. and D.	Change in conductivity. N. and S.	Change in conductivity. K. and D.
10°	57.84	0.01994	316.4	319.1		
					61.2	60.8
20°	57.95	0.02375	377.6	379.9		
					60.0	59.6
30°	58.07	0.02747	437.6	439.5		
10°	251.8	0.004662	322.1	324.5		
					62.3	61.8
20°	252.3	0.005553	384.4	386.3		
					61.3	60.6
30°	252.8	0.006426	445.7	446.9		

It will be seen that our values of the conductivity and those of Kohlrausch and Déguisne agree within 1 per cent., and that the

[1] The same solution was always measured at the three temperatures, the volume being corrected by means of the expansion-coefficient of water.

[2] The conductance at 20° of the resistance-cell when filled with 1/50 molar potassium chloride prepared as directed in Kohlrausch and Holborn's "Leitvermögen der Elektrolyte," page 77, was 0.009116 and 0.009114 respectively before and after the hydrochloric acid measurements. This value was divided into the constant 0.002501 given on page 204, yielding 0.2744 as the cell constant.

[3] Wied. *Ann. Phys.*, 66, 811 (1898).

[4] Kohlrausch and Holborn's "Leitvermögen der Elektrolyte," pp. 11, 199.

changes of conductivity with the temperature agree almost completely. The temperature-coefficient is, moreover, almost exactly the same at the two dilutions when expressed in percentage of the value at 20°; namely, between 10° and 30°, it is, according to our determinations, 1.605 per degree at 1/58 molar, and 1.607 at 1/252 molar.

X. THE EQUIVALENT CONDUCTIVITY OF DISSOCIATED HYDROCHLORIC ACID AND OF THE HYDROGEN ION.

The equivalent conductivity of the chlorine ion at 18° and its temperature-coefficient between 2° and 34° has been calculated by Kohlrausch[1] on the basis of the exact conductivity determinations of Kohlrausch and Maltby on potassium chloride, the temperature-coefficients of Déguisne, and the value 0.503 for the transference number of the anion in potassium chloride. The conductivity values extrapolated for infinite dilution were made the subject of a careful study, and that adopted for potassium chloride is undoubtedly the best that can be obtained. It seems to us desirable, however, to review briefly here the recent determinations of the transference-numbers of potassium chloride, in order to arrive at the best possible value and to form an estimate of its accuracy; especially since new determinations have been published since Kohlrausch's calculations were made. All the recent results (multiplied by 1000) are summarized in the following table.

Investigator.	Temperature.	Dilution in liters.	Number of experiments.	Mean value.	A.D. of mean.
Bein[2]	9°–12°	12–90	3.5[5]	505.1	0.6
Jahn and Bogdan[3] .	18°–19°	30–120	11	503.2	0.5
Steele and Denison[4]		200–400	9	504.8	0.7
			Final mean,	504.4	0.5

As there is no indication that the transference number changes appreciably with the temperature or concentration, we adopt as the most probable value the mean result from these three series of experiments (504.4). We have then multiplied this by Kohlrausch's conductivity values for potassium choride at the three

[1] *Sitzungsber königl. preuss. Akad. der Wiss.*, (1900), p. 1002; (1901), p. 1031.
[2] *Ztschr. phys. Chem.*, 27, 50 (1898).
[3] *Ibid.*, 37, 684 (1901).
[4] *Ibid.*, 40, 753; *Trans. Chem. Soc.*, 81, 468 (1902).
[5] Bein attributes to two of his experiments a weight of 1/4 each.

temperatures. The values[1] so obtained for the chorine ion are:

$$Cl': 54.5 \text{ at } 10°, 68.5 \text{ at } 20°, 83.3 \text{ at } 30°.$$

By combining these values with the final means of our transference experiments with the 1/60 molar hydrochloric acid solution, the following values of the equivalent conductivity, in reciprocal ohms, of completely dissociated hydrochloric acid are obtained:

$$H^{\cdot} + Cl': 343.6 \text{ at } 10°, 409.1 \text{ at } 20°, 469.7 \text{ at } 30°.$$

The accidental errors in these results can be equalized, and a further indication of their magnitude obtained, by calculating from each of the three values the other two by means of the temperature-coefficient of the conductivity of dilute hydrochloric acid. It has already been shown in Section IX that Deguisne's value of this coefficient is in close agreement with our own, and that the coefficient does not change appreciably with the dilution. Employing his value,[1] the following results are obtained, the one which forms the basis of the calculation being printed in italics.

10°.	20°.	30°.
343.6	409.0	473.0
343.7	*409.1*	473.2
341.2	406.1	*469.7*

We assign to the results based upon the 10° and 20° values twice as much weight as to that based upon the 30° value because of their agreement and its divergence, and especially because the transference numbers of potassium chloride were determined between 10° and 20°, and its molar conductivity at infinite dilution was accurately deduced for 18°, the values of these quantities at 30° being based upon the assumption of a temperature-coefficient of zero for the transference-number and upon one for the con-

[1] The transference numbers of sodium chloride furnish an independent means of deriving these conductivities; but these numbers vary with the temperature, and the determinations of them are less numerous. The only ones that are of significance to us are those of Bein around 10°, from which is derived a value at 10°, of 614.9 (A.D. 2.0; 7 experiments) and those of Jahn and Bogdan at 18.5° from which is derived with the help of Bein's temperature-coefficient a value at 20° of 603.3 (A.D. 0.3; 12 experiments). By multiplying Bein's result by Kohlrausch's value of the conductivity at infinite dilution of sodium chloride (89.87) we get 55.3 at 10° for the chlorine ion; but, owing to the large A.D. of the former value, very little weight is to be attached to this result in comparison to that attached to the one from the potassium chloride experiments. From Jahn and Bogdan's transference value we get 68.7 at 20° for the chlorine ion in close agreement with that derived through potassium chloride.

[2] $L_t = L_{18}[1 + 0.0164\,(t-18) - 0.000015\,(t-18)^2]$.

ductivity derived from values less carefully determined than those at 18°. Taking the means under this assignment of weights, and interpolating with the help of Déguisne's temperature-coefficient for 18° and 25°, we get the following final values for the equivalent conductivity in reciprocal ohms of completely dissociated hydrochloric acid and of the hydrogen ion:

	10°.	18°.	20°.	25°.	30°.
$H^{\cdot} + Cl'$.....	343.2	395.5	408.5	440.7	472.4
$H^{\cdot}$	288.7	329.8	340.0	364.9	389.1

XI. PROBABLE ACCURACY OF THE FINAL CONDUCTIVITY VALUES.

Aside from the uncertainty in the assumption that the transference-number of hydrochloric acid has the same value at extreme dilution as at one of 60 liters, a fair estimate can be formed of the probable accuracy of these final results through a consideration of the data upon which they are based. It will be recalled that the three factors involved are the molar conductivity and the transference-number of completely dissociated potassium chloride and the transference-number of 1/60 molar hydrochloric acid: (1) In regard to the first of these, Kohlrausch shows that the formula which he employs for expressing the change of conductivity with the dilution gives interpolated values between 0.1 and 0.0001 molar agreeing with the observed ones within 0.1 per cent. We may therefore estimate that the value extrapolated for zero concentration is probably in error by only a little greater amount, say by 0.2 per cent.; (2) The average deviation of the mean value of the transference-number for potassium chloride from the three series of independent determinations was seen above to be 0.1 per cent.: and as this transference-number shows no variation between 1/12 and 1/400 normal, there is probably no error in the assumption that it has the same value at infinite dilution; (3) The average deviation of the final means of the hydrochloric acid transference number was about 0.1 per cent. From this estimate and these deviations, we find the average deviation or probable error of the final values of the conductivity of $H^{\cdot} + Cl'$ and $H^{\cdot}$ to be 0.25 per cent. Assuming that the actual error in each of the three factors was twice its percentage average deviation, and that the effect of these errors all lay in the same direction, the error in

the final result would be 0.8 per cent. This may be regarded as a limit which it is almost certain is not exceeded by the effect of the errors arising from all sources except the assumption that the hydrochloric acid transference value does not change with the dilution after 60 liters are reached. It is not probable that any considerable error arises through this assumption; but there is a possibility that the final conductivity values are 1 to 2 per cent. too high as a result of it (see Section VIII). The uncertainty can be removed only by transference-determinations at a greater dilution, which will be undertaken in this laboratory as soon as the opportunity offers.

XII. COMPARISON WITH PREVIOUSLY ADOPTED VALUES.

It is of interest to compare our final values with those that have been previously employed. Ostwald[1] estimated ten years ago upon the basis of the then existing conductivity values that the equivalent conductivity at 25° of the hydrogen ion was 345 when expressed in reciprocal ohms; and it is this value that has been used in almost all the calculations of the dissociation and the dissociation-constants of acids. The value to which this investigation has led is, however, 365, which is 5.8 per cent. higher than that commonly employed.

Kohlrausch[2] has very recently adopted 318 as the most probable value at 18°. Our value is 330, which is greater by 3.8 per cent.

In spite of the fact that a small degree of uncertainty attaches to our results for the reason stated in the preceding section, we believe that they rest upon a more satisfactory foundation than do the older ones, which were based upon an almost unguided extrapolation from the conductivity-values of acids.

BOSTON, MASS., July, 1902.

[1] "Lehrbuch der allgemeinen Chemie," Vol. II, part 1, p. 675.

[2] *Sitzungsber. der königl. preuss. Akad. der. Wiss.*, (1902), p. 1031.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.]

SOME PRELIMINARY EXPERIMENTS UPON THE CLINKERING OF PORTLAND CEMENT.

BY E. D. CAMPBELL.

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AS THE work which was begun in this laboratory about three years ago on the constitution of hydraulic cements progressed, it became more and more evident that if real progress was to be made in our knowledge of cements, the various factors entering into the problem must be considered separately. The experiments described in the present paper were performed by Messrs. C. A. Burck, A. G. Smith and W. B. Cady, and I wish here to acknowledge my indebtedness to them for the care with which they have carried on the work. The object of these preliminary experiments was to furnish a basis on which a complete series of experiments could be based which should show the exact relation between the chemical composition of a slurry and the temperature required for burning. When the exact influence of each constituent upon the property of a clinker produced at a given temperature has been determined, we may then begin to study systematically the influence of variations in mechanical treatment, subsequent to the formation of the clinker, on the properties of the finished cement.

The influence of the many factors such as fineness of grinding, ageing, per cent. of gypsum used, and the method of mixing and working, which come into play after the clinkering is completed, has been studied by others much more carefully than has the influence of each factor which determines the constitution of the clinker. Of these latter factors those which must be considered are: silica free or combined, alumina, ferric oxide, calcium oxide, magnesium oxide, the fineness of division and physical state of the raw material, the temperature, the atmosphere within the furnace whether oxidizing or reducing, and the time during which the material is under treatment. So far as we are aware the only experimental work which has been done to determine the relation of the chemical composition of the material under treatment and the temperature employed in burning, is that of A. Meyer, *Thonindustrie Zeitung*, 73, 1201, abstracted by S. B. Newberry in

Cement, **2**, 350. Meyer's results, which were obtained by most careful and painstaking experiments, illustrate better the conditions found in fixed kilns than in the rotary furnaces so generally used in this country. Meyer made three mixtures and burned each mixture nominally at four different temperatures. The material for each burning was placed in a stationary furnace and raised by means of a gas burner to a specified temperature which was indicated by means of a Seger cone. No statement is made as to the length of time during which the material was heated or whether any means were employed to show variations, especially lowering of the temperature below the maximum indicated by the cones during the burning. In heating a considerable mass of material in a stationary furnace it would be extremely difficult if not impossible to have all the material obtain the same temperature for the same length of time. Possibly Meyer's results would represent those obtained from clinker, part of which had not attained the temperature indicated. It was on account of this difficulty, amounting almost to impossibility of heating a mixture in a stationary furnace uniformly and for the same length of time, that the fixed form of furnace was abandoned in this laboratory and a rotary kiln devised. A detailed description of the rotary kiln employed in the work described in this paper, will be found in this Journal, **24**, 248.

In the experiments herein described we have tried to pay close attention to all the factors which might enter into the formation of the clinker. All raw material was carefully dried and ground fine enough to pass a 100-mesh sieve, the thoroughly dried finely ground material was analyzed, and from materials thus prepared the various mixtures used in the different experiments were made and the composition of the resulting clinker calculated. The composition of the dried materials used is given in the following table:

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Loss on ignition.
Art. clay	67.95	15.76	5.64	1.19	2.02	5.22
Pen. clay.....	64.90	18.06	3.47	2.34	1.34	9.06
Syn. clay.....	55.32	11.78	21.53	2.43	1.82	6.72
No. 3 shale.....	53.05	26.59	5.87	1.84	1.51	9.87
Kaolin	47.35	36.66	1.85	0.40	0.25	12.50
L. W. marl.....	1.21	0.25	0.25	52.89	0.89	44.58

The slurries for burning were all prepared in as nearly the same way as possible, following the method given in the description of the rotary kiln referred to above. The marl required for 100 grams of clay or shale was calculated in each case and sufficient of each taken to make from 4 to 5 kilograms of dried slurry. The clay or shale was disintegrated with an amount of water equal to that of the dry materials and the marl then stirred in. This slurry was then evaporated with frequent stirring to the proper consistency for rolling out and cutting into cubes for drying.

In order to control the temperature the pressure in the gasoline tank was maintained steadily throughout the work between 48 and 50 pounds. When the pyrometer indicated that the furnace was at the lowest temperature at which it was desired to begin to collect clinker, feeding was begun. A number of experiments having shown that with 50 pounds' pressure in the gasoline tank the maximum temperature was about 35° C. higher than that recorded by the stationary couple used in controlling the temperature, the temperatures given in the following tables are all those of this hottest zone, that is, 35° C. higher than was actually measured by the stationary couple. The thermocouple used in this work was calibrated by direct comparison with a similar couple whose electromotive force was certified by the physikalisch-technische Reichsanstalt. From time to time the couple was tested for constancy of electromotive force. The electromotive force of the couple did not change until after Experiment 98, when a temperature of 1618° C. actual having been attained, the wires became somewhat roughened and the electromotive force lowered but remained constant during the next three experiments. When it became necessary after Experiment 101 to replace the porcelain insulating tubing, an entire new couple was made with an electromotive force practically equal to that of the original couple.

When the rotary is making a single revolution in about one minute and twenty-five seconds and has a pitch of 6 per cent., the first pieces of clinker usually come through the furnace in from twenty-five to thirty minutes. This is not, however, the real time of passage, for these first pieces have nothing to impede their progress and pass through the furnace more quickly than when the furnace is fully charged. The real time of passage was

determined by making a very basic slurry with pure kaolin and introducing single pieces of this slurry at intervals of about fifteen minutes during the burning of one of the slurries containing considerable ferric oxide. The clinker resulting from the kaolin being different in color from the rest was readily recognized and the average time of passage of these pieces was found to be about one hour and fifteen minutes. When the speed of the rotary was reduced so that a single revolution required two minutes and forty-five seconds, the time of passage was increased to an average of two hours and nineteen minutes. In the following experiments those which were made with the higher speed and shorter time of passage are marked only with a number, while those made with the slower speed and longer time of passage are indicated by a letter, A, following the number; thus Experiment 94A was made with the same slurry, etc., as Experiment 94, but with longer time of burning.

When from 80 to 100 grams of clinker had been collected at a given temperature, kept constant within 5° or less, the temperature was raised from 22° to 30° C. and kept constant for ten minutes before commencing to collect another sample. In this way a series of samples was collected at gradually increasing temperatures until the "overburning" temperature was attained. By the term "overburning temperature" is here meant that temperature at which the individual pieces of clinker begin to stick together or ball-up. This is the highest temperature at which samples can be collected. Experiment 98 was the only one of this series in which this overburning temperature was not reached. The progressive changes of appearance of the clinkers with increase of temperature are quite marked even for the comparatively small intervals of temperature. All the pieces produced at the same temperature are practically identical in appearance but in most cases the successive samples are readily distinguished from each other. With increasing temperature the material passes gradually from white or nearly white to deep brown or nearly black in color with marked contraction in volume as the sintering becomes more and more complete until the clinker produced at the highest temperature has a more or less glazed appearance as distinguished from the dull color of the preceding sample.

It was noticed during some of the experiments that if the per

cent. of carbon monoxide in the escaping gases was allowed to exceed 0.3 per cent., the clinker assumed a yellowish brown color instead of the familiar deep brown or black of properly burned clinker, and the cement produced from it was off color instead of the normal color of good cement. The extent to which the chemical composition of the clinker is altered by carbon monoxide has not been thoroughly investigated as yet but we hope to do some more work on this question at a later date.

It was thought that a measure of the volume occupied by 1 gram of the clinker would be a much better indication of the shrinkage due to the sintering of the material than a determination of the specific gravity of the powdered material; this "volume per gram" of the clinker was measured in the following way and is given in the table under the various experiments. About ten grams of unbroken pieces of clinker were placed in a small flask containing sufficient glycerine to cover the pieces and the flask was then attached to an aspirator and exhausted until the pores of the clinker were filled with glycerine. A burette was filled with glycerine to within 10 cc. of the zero point. The pieces of clinker were then removed from the flask and wiped lightly on the outside with a cloth saturated with glycerine, and these pieces of clinker with the pores filled with glycerine were then dropped into the burette and the volume of glycerine displaced read off and calculated to the "volume per gram" of the clinker. As soon as the volume displaced by the first sample has been determined, enough glycerine may be drawn off to again bring the level of the glycerine to the starting point and the volume of the second sample determined without removing the first and so on until the burette is full. This method of determining the volume per gram, and hence the shrinkage, gives rapid and much more satisfactory results than are obtained by determining the specific gravity of the powder.

All samples of clinker after collecting were kept in tightly stoppered bottles until ready for grinding and making pat tests which was usually done within two or three days from the time of burning. A portion of the crushed clinker was mixed in most cases with 2 per cent. of plaster of Paris, although in a few instances 3 per cent. had to be used. The amount employed is given under each experiment. After mixing with the plaster of Paris the

clinker was ground until all of it would pass a 100-mesh sieve. The per cent. of water required for normal consistency was determined by adding water to a weighed amount of the cement with thorough mixing until a ball of the material about one-half inch in diameter when dropped from a distance of about 12 inches would flatten slightly but would not crack. The time of setting was determined upon pats made with the required amounts of water using needles of $^1/_{12}$ and $^1/_{24}$ inch in diameter weighted with $^1/_4$ and 1 pound respectively for initial and final sets. The time of the initial and final set was taken as that when the above needles just failed to make an impression on the pat. Unless care is used to have the glass on which pats are made strictly clean a pat will often come loose which would otherwise adhere and give a perfect boiling test. The boiling test was made on pats which had stood twenty-four hours in a damp atmosphere. They were placed in a frame supported in a continuous water-bath; the bath was then lighted and the water brought to the boiling-point and kept boiling for twenty-four hours when the pats were removed and, after cooling, examined. The details of the influence of temperature upon shrinkage, amount of water required, time of setting and boiling tests upon various mixtures are given in the following tables under the various experiment numbers. The proportion of clay or shale, and marl used in each mixture and the molecular formula of the clinker reduced to a basis of 100 molecules of silica in each case is also given.

TABLE I.—EXPERIMENT 103.

	Grams.
Art. clay	100
L. W. Marl	275

Composition of clinker: SiO_2, 28.83; Al_2O_3, 6.65; Fe_2O_3, 2.15; CaO, 59.61; MgO, 1.80.

Molecular formula: $100(1.868\,CaO,\ 0.091\,MgO,\ SiO_2) + 13.4(2\,CaO.Al_2O_3) + 2.8(2\,CaO.Fe_2O_3)$.

Eight samples of clinker collected and ground with 3 per cent. plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Per cent. water.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1395	0.78	27	14	310	Badly warped, one crack, weak.
2	1419	0.76	27	11	276	Badly warped, large cracks, weak.
3	1443	0.74	25	10	208	Slightly warped, no cracks, strong.
4	1467	0.64	24	9	14	Perfect.
5	1493	0.60	24	5	12	Perfect.
6	1515	0.55	24	10	25	Perfect.
7	1537	0.46	24	7	35	Perfect.
8	1549	0.38	24	6	25	Perfect.

TABLE II.—EXPERIMENT 98.

	Grams.
Art. clay	100
L. W. marl	339.3

Composition of clinker : SiO_2, 25.48; Al_2O_3, 5.87; Fe_2O_3, 2.29; CaO, 63.87; MgO, 1.79.

Molecular formula: $100(2.347\,CaO, 0.105\,MgO, SiO_2) + 13.5(2CaO.Al_2O_3) + 3.4(2\,CaO.Fe_2O_3)$.

Fourteen samples of clinker collected and ground with 2 per cent. plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1353	0.65	30	165	193	Disintegrated.
2	1381	0.65	30	110	260	Expanded over edge of glass, easily rubbed to sand.
3	1405	0.65	29	91	246	Not warped, expanded, rather weak.
4	1427	0.61	29	100	290	Slightly warped, moderately expanded, rather weak.
5	1456	0.60	28	97	300	Moderately warped, no cracks, strong.
6	1475	0.59	27	80	300	Moderately warped, no cracks, strong.
7	1498	0.56	27	90	300	Slightly warped, no cracks, very strong.
8	1521	0.55	25	91	306	Loose from glass, free from cracks, very strong.
9	1545	0.54	25	84	330	Perfect.
10	1567	0.53	25	60	240	Off color due to carbon monoxide.
11	1589	0.55	25	58	264	Perfect.
12	1611	0.50	25	57	359	Perfect.
13	1633	0.50	25	65	356	Perfect.
14	1653	0.45	25	59	361	Perfect.

TABLE III.—EXPERIMENT 87.

	Grams.
Pen. clay	100
L. W. marl	271.3

Composition of clinker: SiO_2, 28.26; Al_2O_3, 7.77; Fe_2O_3, 1.72; CaO, 60.44; MgO, 1.51.

Molecular formula: $100(1.90\ CaO, 0.079\ MgO, SiO_2) + 16(2\ CaO.Al_2O_3) + 2.3(2\ CaO.Fe_2O_3)$.

Seven samples of clinker collected and ground with 3 per cent. plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1337	...	36	12	31	No cracks, quite strong.
2	1365	...	34	24	355	Fine cracks, quite weak.
3	1389	...	27	18	276	Disintegrated.
4	1417	...	25	152	187	Very badly warped, cracked, easily rubbed to sand.
5	1441	...	24	214	259	Warped, deep cracks, but very strong.
6	1467	...	24	204	254	Perfect.
7	1491	...	24	35	65	Perfect.

Nos. 1 and 2 were loose from glass six hours after making.

Made a set of pats with 2 per cent. of plaster of Paris as follows:

Sample num	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1337	...	34	10	45	Fine hair cracks, moderately strong.
2	1365	...	31	10	35	Fine hair cracks, not quite as strong as No. 1.
3	1389	...	25	10	27	Disintegrated.
4	1417	...	24	8	23	Disintegrated.
5	1441	...	24	5	6	Loose from glass, badly warped.
6	1467	...	24	5	10	Perfect.
7	1491	...	24	5	11	Perfect.

Nos. 1 and 2 were loose from glass eight hours after making.

TABLE IV.—EXPERIMENT 88.

	Grams.
Pen. clay	100
L. W. marl	301.85

Composition of clinker: SiO_2, 26.51; Al_2O_3, 7.28; Fe_2O_3, 1.63; CaO, 62.73; MgO, 1.56.

Molecular formula: 100(2.137 CaO, 0.088 MgO,SiO_2) + 16.1(2 CaO.Al_2O_3) + 2.3(2 CaO.Fe_2O_3).

Nine samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1343	0.83	34	9	13	Somewhat warped, fine cracks, rather weak.
2	1363	0.77	30	10	12	Disintegrated.
3	1407	0.66	26	8	15	Disintegrated.
4	1431	0.61	25	60	100	Badly warped, easily rubbed to sand.
5	1453	0.51	24	89	189	Badly warped, fine cracks, moderately strong.
6	1463	0.44	24	94	229	Loose from glass, slightly warped, no cracks, very strong.
7	1507	0.41	24	100	240	Loose from glass, not warped, no cracks, very strong.
8	1533	0.41	23	102	312	Perfect.
9	1553	0.39	23	137	250	Perfect.

Nos. 1 and 2 were loose from glass six hours after making.

TABLE V.—EXPERIMENT 97.

	Grams.
Syn. clay	100
L. W. marl	298.7

Composition of clinker: SiO_2, 22.76; Al_2O_3, 4.80; Fe_2O_3, 8.61; CaO, 61.97; MgO, 1.73.

Molecular formula: 100(2.393 CaO, 0.113 MgO, SiO_2) + 12.4(2 CaO.Al_2O_3) + 13.7(2 CaO.Fe_2O_3).

Twelve samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1285	0.93	56	4	63	Slightly warped away from glass, fine cracks, weak.
2	1309	0.92	45	5	66	Slightly warped away from glass, quite strong.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
3	1335	0.75	35	4	9	Slightly warped away from glass, cracked, very weak.
4	1359	0.75	30	5	10	Badly disintegrated.
5	1383	0.70	30	34	122	Very badly disintegrated.
6	1407	0.68	28	56	440	Somewhat warped, badly scaled, weak.
7	1431	0.60	25	40	436	Moderately warped, numerous cracks, strong.
8	1455	0.52	24	120	434	Perfect.
9	1479	0.50	23	32	375	Perfect.
10	1505	0.47	21	105	315	Perfect.
11	1526	0.41	21	95	345	Perfect.
12	1549	0.38	21	81	341	Perfect.

TABLE VI.—EXPERIMENT 102A.

	Grams.
No. 3 shale	100
L. W. marl	124.7
MgO	82.8, added in the form of pure magnesium carbonate.

Composition of clinker: SiO_2, 22.53; Al_2O_3, 11.11; Fe_2O_3, 2.55; CaO, 28.00; MgO, 35.28.

Molecular formula: $100(CaO, 2MgO,SiO_2) + 29(CaO.MgO.Al_2O_3) + 4.2(CaO.MgO.Fe_2O_3)$.

Six samples of clinker collected and ground with 3 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1321	0.86	40	20	55	Loose, free from cracks, moderately strong.
2	1347	0.84	39	26	..	Loose, free from cracks, weak.
3	1373	0.82	33	22	..	Loose, free from cracks, rather weak.
4	1395	0.80	34	33	..	Loose, free from cracks, rather weak.
5	1423	0.68	32	1232	..	Loose, free from cracks, rather weak.
6	1445	0.44	29	120	..	Loose, free from cracks, rather weak.

Nos. 2, 3, 4, 5, and 6 were not set after nine hours; No. 2 was set after eighteen hours; Nos. 3, 4, and 6 set after twenty-two hours; No. 5 was not set after twenty-four hours.

This cement even after long setting appeared to crumble more or less under the fine needle, instead of becoming firm as with most hydraulic cements.

TABLE VII.—EXPERIMENT 92.

	Grams.
No. 3 shale	100
L. W. marl	250.1

Composition of clinker: SiO_2, 24.51; Al_2O_3, 11.90; Fe_2O_3, 2.84; CaO, 58.63; MgO, 1.64.

Molecular formula: $100(1.905\ CaO, 0.10\ MgO, SiO_2) + 28.5(2CaO.Al_2O_3) + 4.3(2CaO.Fe_2O_3)$.

Six samples of clinker collected and ground with 3 per cent. plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1336	0.84	40	15	25	Rather weak.
2	1361	0.835	35	20	105	Loose from glass, rather weak.
3	1391	0.75	30	57	107	Loose from glass, badly warped, cracked, very weak.
4	1415	0.55	24	100	145	Very badly warped, cracked, easily rubbed to sand.
5	1427	0.41	24	118	148	Very badly warped, cracked, rather weak.
6	1438	0.39	25	2	6	Loose from glass, free from cracks, strong.

No. 1 was loose from glass three hours after making.

TABLE VIII.—EXPERIMENT 92A.

Composition identical with Experiment 92, the only difference being increased time of passage of material through the furnace.

Four samples of clinker were collected and ground with 3 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1359	0.69	30	50	225	Very badly warped, cracked, rather easily rubbed to sand.
2	1383	0.65	27	145	220	Very badly warped, cracked, easily rubbed to sand.
3	1407	0.44	25	145	165	Very badly warped, cracked, rather weak.
4	1431	0.40	24	155	205	Loose from glass, free from cracks, strong.

TABLE IX.—EXPERIMENT 95A.

	Grams.
No. 3 shale	100
L. W. marl	250.1
MgO	18.45, added as

pure magnesium carbonate.

Composition of clinker: SiO_2, 22.77; Al_2O_3, 11.05; Fe_2O_3, 2.64; CaO, 54.47; MgO, 9.01.

Molecular formula: $100(1.907\ CaO, 0.589\ MgO, SiO_2) + 28.5(2CaO.Al_2O_3) + 4.3(2CaO.Fe_2O_3)$.

Six samples of clinker collected and ground with 3 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1335	0.89	38	6	19	Cracked, rather weak.
2	1359	0.72	34	12	230	Very badly warped, cracked, very weak.
3	1383	0.69	32	38	292	Very badly warped, easily rubbed to sand.
4	1405	0.52	30	148	313	Very badly warped, very easily rubbed to sand.
5	1431	0.47	25	45	195	Free from cracks, slightly warped, quite weak.
6	1455	0.39	25	6	10	Firmly adherent to glass, but rather weak.

No. 1 was loose from glass before submitting to boiling test.

TABLE X.—EXPERIMENT 93.

	Grams.
No. 3 shale	100
L. W. marl	275.3

Composition of clinker: SiO_2, 23.19; Al_2O_3, 11.24; Fe_2O_3, 2.70; CaO, 60.75; MgO, 1.63.

Molecular formula: $100(2.148\ CaO, 0.105\ MgO, SiO_2) + 28.4(2CaO.Al_2O_3) + 4.4(2CaO.Fe_2O_3)$.

Eight samples of clinker collected and ground with 3 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1331	0.94	55	10	13	Not cracked, very weak.
2	1357	0.93	50	8	21	Not cracked, very weak.
3	1383	0.87	40	7	8	Loose from glass, no cracks, stronger than No. 2.
4	1407	0.82	35	8	23	Warped, moderately cracked, very weak.
5	1431	0.72	32	18	192	Disintegrated.
6	1455	0.58	28	20	192	Disintegrated.
7	1481	0.51	24	85	205	Loose from glass, free from cracks, very strong.
8	1503	0.41	24	75	205	Perfect.

Nos. 1 and 2 were loose from glass before submitting to boiling test.

TABLE XI.—EXPERIMENT 101.

	Grams.
No. 3 shale	100
L. W. marl	294.4

Composition of clinker: SiO_2, 22.35; Al_2O_3, 10.79; Fe_2O_3, 2.60; CaO, 62.22; MgO, 1.63.

Molecular formula: $100(2.328\,CaO, 0.109\,MgO, SiO_2) + 28.3(2CaO.Al_2O_3) + 4.4(2CaO.Fe_2O_3)$.

Five samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1463	0.60	28	105	134	Disintegrated.
2	1487	0.57	28	80	140	Disintegrated.
3	1511	0.55	25	138	156	Perfect.
4	1535	0.51	24	76	139	Perfect.
5	1557	0.42	24	135	240	Off color, loose from glass, warped, cracked.

No. 1 was loose from glass before submitting to boiling test.

TABLE XII.—EXPERIMENT 94.

	Grams.
No. 3 shale	100
L. W. marl	300.8

Composition of clinker : SiO_2, 22.07; Al_2O_3, 10.64; Fe_2O_3, 2.57; CaO, 62.64; MgO, 1.59.

Molecular formula : $100(2.385\ CaO, 0.107\ MgO, SiO_2) + 28.3(2CaO.Al_2O_3) + 4.4(2CaO.Fe_2O_3)$.

Ten samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1359	0.89	60	38	360	Loose from glass, fine cracks, rather weak.
2	1383	0.87	55	10	65	Loose from glass, fine cracks, rather weak.
3	1407	0.80	47	5	33	Badly warped, cracked, difficultly rubbed to sand.
4	1431	0.71	40	5	33	Disintegrated.
5	1455	0.66	30	65	80	Disintegrated.
6	1478	0.54	25	87	105	Warped from glass, cracked, very weak.
7	1501	0.50	24	94	100	Loose from glass, sound, very strong.
8	1525	0.496	23	85	101	Loose from glass, sound, very strong.
9	1549	0.42	23	105	165	Perfect.
10	1573	0.40	23	140	255	Perfect.

Nos. 4 and 5 were loose from glass before submitting to boiling test.

TABLE XIII.—EXPERIMENT 94A.

Composition identical with Experiment 94, the only difference being due to increased time of passage of material through the furnace.

Nine samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set Minutes.	Final set. Minutes.	Boiling test.
1	1359	0.78	35	5	8	Very badly cracked, easily rubbed to sand.
2	1383	0.67	34	15	20	Very soft, almost completely disintegrated.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
3	1407	0.66	30	52	62	Very soft, almost completely disintegrated.
4	1431	0.60	26	66	81	Very badly warped, cracked, easily rubbed to sand.
5	1455	0.50	25	86	116	Warped away from glass, free from cracks, very strong.
6	1478	0.49	24	109	154	Perfect.
7	1501	0.45	24	146	284	Perfect.
8	1525	0.44	23	120	260	Perfect.
9	1545	0.40	23	108	240	Perfect.

No. 1 was loose from glass before submitting to boiling test.

TABLE XIV.—EXPERIMENT 96A.

	Grams.
No. 3 shale	100
L. W. marl	300.8
MgO	18.45, added as pure magnesium carbonate.

Composition of clinker: SiO_2, 20.59; Al_2O_3, 9.94; Fe_2O_3, 2.40; CaO, 58.45; MgO, 8.22.

Molecular formula: $100(2.387\,CaO, 0.594\,MgO, SiO_2) + 28.3(2CaO.Al_2O_3) + 4.4(2CaO.Fe_2O_3)$.

Ten samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1361	0.73	36	3	5	Very badly broken, almost disintegrated.
2	1389	0.69	34	4	10	Disintegrated.
3	1411	0.61	29	65	79	Disintegrated.
4	1437	0.59	26	94	154	Very badly warped, large cracks, quite weak.
5	1463	0.52	25	116	216	Warped, fine radical cracks, strong.
6	1487	0.44	25	125	260	Perfect.
7	1509	0.44	24	140	294	Perfect.
8	1535	0.44	23	105	269	Perfect.
9	1557	0.41	23	92	212	Perfect.
7A	1519	0.41	23	92	240	Perfect.

During the collection of sample 7A an excess of gasoline was admitted into the furnace, the products of combustion showing carbon dioxide, 9 per cent., oxygen, 0.20 per cent., and carbon monoxide, 9.3 per cent. The cement produced was yellowish in color instead of the usual color of good cement.

TABLE XV.—EXPERIMENT 99.

	Grams.
No. 3 shale	100
L. W. marl	318.14

Composition of clinker: SiO_2, 21.34; Al_2O_3, 10.28; Fe_2O_3, 2.50; CaO, 63.83; MgO, 1.62.

Molecular formula: $100(2.54\,CaO, 0.113\,MgO, SiO_2) + 28.3(2CaO.Al_2O_3) + 4.4(2\,CaO.Fe_2O_3)$.

Eight samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1447	0.67	43	3	5	Completely disintegrated.
2	1473	0.63	37	13	15	Completely disintegrated.
3	1497	0.55	29	13	14	Completely disintegrated.
4	1523	0.52	25	100	204	Cracked, expanded, slightly warped, very weak.
5	1545	0.50	25	96	201	Expanded, badly warped, very weak.
6	1587	0.49	24	120	265	Warped, free from cracks, very strong.
7	1593	0.43	24	96	219	Loose from glass, very strong.
8	1613	0.40	23	94	304	Loose from glass, very strong.

TABLE XVI.—EXPERIMENT 100.

	Grams.
No. 3 shale	100
L. W. marl	353.6

Composition of clinker: SiO_2, 20.07; Al_2O_3, 9.61; Fe_2O_3, 2.36; CaO, 66.12; MgO, 1.63.

Molecular formula: $100(2.881\,CaO, 0.121\,MgO, SiO_2) + 28.1(2CaO.Al_2O_3) + 4.4(2CaO.Fe_2O_3)$.

Eight samples of clinker collected and ground with 2 per cent. of plaster of Paris.

Sample number.	Maximum temperature.	Volume per gram.	Water. Per cent.	Initial set. Minutes.	Final set. Minutes.	Boiling test.
1	1461	0.60	28	120	198	Completely disintegrated.
2	1485	0.55	28	128	218	Almost disintegrated.
3	1509	0.51	25	105	205	Very badly broken.
4	1529	0.50	25	122	242	Badly warped, much expanded, very weak.
5	1555	0.49	25	129	240	Badly warped, much expanded, very weak.
6	1581	0.46	25	167	247	Badly warped, much expanded, very weak.
7	1599	0.44	25	153	243	Moderately warped, free from cracks, very strong.
8	1625	0.41	24	140	245	Warped, free from cracks, very strong.

No. 1 was loose from glass before submitting to boiling test.

TABLE XVII.—EXPERIMENT 86.

	Grams.
Kaolin	100
L. W. marl	387.24

Composition of clinker: SiO_2, 17.27; Al_2O_3, 12.45; Fe_2O_3, 0.93; CaO, 67.92; MgO, 1.23.

Molecular formula: $100(2.884\,CaO, 0.106\,MgO, SiO_2) + 42.3(3CaO.Al_2O_3) + 2(3CaO.Fe_2O_3)$.

The separate samples were not collected in this case, but the over-burning temperature was found to be 1571° C. After determining the overburning point the temperature was dropped to 1549° C. and a single large sample collected. This sample ground with 1.5 per cent. of plaster of Paris required 30 per cent. of water, gave an initial set of five minutes and a final set of nine minutes. On submitting the pat to the boiling test, it warped loose from glass, cracked, and was easily rubbed to sand.

The phenomena connected with the time of setting of these cements will not be discussed in this paper but will be reserved for further study. The amount of plaster of Paris was in all cases 2 per cent. except where the small amount of calcium oxide in the cement made 3 per cent. necessary in order to retard the setting sufficiently to obtain measurements. The contraction of the material during burning, as shown in the tables under volume per

TABLE XVIII.

Exp.	Calculated percentage composition of clinker.					Molecular ratios calculated to basis of 100 molecules SiO_2.					Molecular ratio of RO bases to 100 molecules $SiO_2 + Al_2O_3 + Fe_2O_3$.			
	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	$SiO_2 + Al_2O_3 + Fe_2O_3$.	CaO.	MgO.	CaO + MgO.
	Art clay													
103	28.83	6.65	2.15	59.61	1.80	100.0	13.4	2.8	219.2	9.1	100.0	188.6	7.8	196.4
98	25.48	5.87	2.29	63.87	1.79	100.0	13.5	3.4	268.5	10.5	100.0	229.7	8.9	238.6
	Pen clay													
87	28.26	7.77	1.72	60.44	1.51	100.0	16.0	2.3	226.6	7.9	100.0	191.6	6.7	198.3
88	26.51	7.28	1.63	62.73	1.56	100.0	16.1	2.3	253.5	8.8	100.0	214.1	7.4	221.5
	Syn. Clay A (Art Clay + $Fe(OH)_3$)													
97	22.76	4.80	8.61	61.97	1.73	100.0	12.4	13.7	291.5	11.3	100.0	231.2	8.9	240.1
	No. 3 Shale													
102A	22.53	11.11	2.55	28.00	35.28	100.0	29.0	4.2	133.1	232.9	100.0	100.0	174.7	274.7
92	24.51	11.90	2.84	58.63	1.64	100.0	28.5	4.3	256.1	10.0	100.0	192.8	7.5	200.3
92A	24.51	11.90	2.84	58.63	1.64	100.0	28.5	4.3	256.1	10.0	100.0	192.8	7.5	200.3
95A	22.77	11.05	2.64	54.47	9.01	100.0	28.5	4.3	256.3	58.9	100.0	192.9	44.3	237.2
93	23.19	11.24	2.70	60.75	1.63	100.0	28.4	4.4	280.4	10.5	100.0	211.1	7.9	219.0
101	22.35	10.79	2.60	62.22	1.63	100.0	28.3	4.4	298.2	10.9	100.0	224.7	8.2	232.9
94	22.07	10.64	2.57	62.64	1.59	100.0	28.3	4.4	303.9	10.7	100.0	228.8	8.1	236.9
94A	22.07	10.64	2.57	62.64	1.59	100.0	28.3	4.4	303.9	10.7	100.0	228.8	8.1	236.9
96A	20.59	9.94	2.40	58.45	8.22	100.0	28.3	4.4	304.1	59.4	100.0	229.1	44.7	273.8
99	21.39	10.28	2.50	63.83	1.62	100.0	28.3	4.4	319.4	11.3	100.0	240.8	8.5	249.3
100	20.07	9.61	2.36	66.12	1.63	100.0	28.1	4.4	353.1	12.1	100.0	266.4	9.1	275.5
	Kaolin													
86	17.27	12.75	0.93	67.92	1.25	100.0	42.3	2.0	421.3	10.6	100.0	291.7	7.3	299.0
	Results of Meyer's experiments													
M. 1	23.20	11.40	2.50	61.50	2.70	100.0	28.8	4.0	285.1	17.3	100.0	214.6	13.0	227.6
M. 2	22.10	9.70	2.40	63.30	2.40	100.0	26.1	4.1	310.8	16.4	100.0	238.7	12.5	251.2
M. 3	20.90	8.80	2.20	65.50	2.30	100.0	24.7	3.9	335.6	16.4	100.0	260.7	12.8	273.5

TABLE XVIII (*Continued*).

Exp.	Ratios of atoms of oxygen in RO bases to 100 atoms of oxygen in $SiO_2 + Al_2O_3 + Fe_2O_3$.				Temperatures. Degrees Centigrade.			Percentage of water required for normal consistency		
	$SiO_2 + Al_2O_3 + Fe_2O_3$.	CaO.	MgO.	CaO + MgO.	Maximum disintegration.[1]	First perfect boiling-test.[2]	Over-burning temperature.[3]	Maximum disintegration.[1]	First perfect boiling-test.[2]	Over-burning temperature.[3]
	Art clay									
103	100.0	88.1	3.5	91.6	1419	1467	1549	27	24	24
98	100.0	107.1	4.2	111.3	1353	1545	above 1653	30	25	25
	Pen clay									
87	100 0	88.8	3.1	91.9	1389	1467	1491	25	24	24
88	100.0	99.3	3.4	102.7	1363	1533	1553	30	23	23
	Syn. Clay A (Art Clay + $Fe(OH)_3$)									
97	100.0	104.7	4.1	108.8	1359	1455	1549	30	24	21
	No. 3 Shale									
102A	100.0	44.3	77.7	122.0	None[4]	None[4]	1445	..[4]	..[4]	29
92	100.0	85.8	3.3	89.1	1415	1438[5]	1438	24	25[5]	25
92A	100.0	85.8	3.3	89.1	1383	1431[5]	1431	27	24[5]	24
95A	100.0	85.8	19.7	105.5	1383	1455	1455	32	25	25
93	100.0	93.9	3.5	97.4	1431	1503	1503	32	24	24
101	100.0	100.0	3.9	103.9		1511	1557	..	25	24
94	100.0	101.9	3.6	104.5	1431	1549	1573	40	23	23
94A	100.0	101.9	3.6	104.5	1383	1478	1545	34	24	23
96A	100.0	102.0	19.9	121.9	1389	1487	1557	34	25	23
99	100.0	107.3	3.7	111.0		1593[5]	1613	..	24[5]	23
100	100.0	118.6	4.1	122.7		None	1625	..	..	24
	Kaolin									
86	100.0	126.5	3.2	129.7		None	1571	..	..	..
	Results of Meyer's experiments									
M. 1	100.0	95.5	4.3	99.7	1370?	1550?		..	..	..
M. 2	100.0	106.9	5.6	112.5	1370?	1490?		..	..	.
M. 3	100.0	117.8	5.7	123.5	1370	None		..	..	..

[1] By temperature of maximum disintegration is meant the temperature at which that clinker was produced which, when made into pats, showed the greatest disintegration in boiling water.

[2] By temperature of first perfect boiling-test is meant the lowest temperature at which clinker was produced which, when made into pats, remained strong, free from cracks, and firmly adherent to the glass after exposure to boiling water for twenty-four hours.

[3] By over-burning temperature is meant the lowest point during the burning at which the individual pieces of clinker commenced to stick badly to each other or to the inside of the furnace.

[4] These pats were all free from cracks but rather weak.

[5] These pats were strong, free from cracks, not warped, but loose from glass.

gram, increases in all cases with increasing temperature up to the highest temperature attained. At the overburning temperature the volume per gram for all ordinary cements lies within the narrow limits of 0.38-0.42 cc. per gram.

We desire to discuss more fully the phenomena connected with the clinkering as indicated by the soundness of the cement shown by the boiling test. For that purpose we have summarized the more important data in Table XVIII, and have included some results given by Meyer which we have recalculated to the same basis as our own. A comparative study of the soundness of the pats after having been subjected to the action of boiling water for twenty-four hours shows most clearly the relation existing between the chemical composition and temperature of burning. In any series the successive pats show differences in behavior in boiling water. If the collection be begun below about 1250° C. the first pats will come loose from the glass soon after making but will become quite strong and remain sound and free from cracks under the boiling test. As the temperature of burning rises, the pats begin to crack more and more, then go to pieces and finally nearly or quite completely disintegrate. With further increase of burning temperature the extent of disintegration diminishes until, if the cement is properly proportioned, the pats again become sound and strong, remaining firmly attached to the glass. Further increase of temperature does not affect the soundness of the pat unless carbon monoxide is present in the furnace gases. In this case the pat may come loose from the glass but will still remain sound and strong.

For purposes of study, three points have been selected as indicating important changes in clinker. Such changes in condition of clinker may indicate formation of definite chemical compounds or changes in the phases of a solid solution. The three points selected are: 1, *temperature of maximum disintegration* by which is meant the temperature at which that clinker was produced which, when made into pats, showed the greatest disintegration in boiling water; 2, *temperature of perfect boiling test,* by which is meant the lowest temperature at which clinker was produced which, when made into pats, remained strong, free from cracks and firmly adherent to the glass after exposure to boiling water for twenty-four hours; 3, *overburning temperature* by which is

meant the lowest point during the burning at which the individual pieces of clinker commenced to stick badly to each other or to the inside of the furnace.

The influence of chemical composition will be discussed with reference to these three temperatures.

TEMPERATURE OF MAXIMUM DISINTEGRATION.

For a given clay the ratio CaO to $SiO_2 + Al_2O_3$ must reach a certain magnitude before the pats will completely disintegrate. Experiments 103, 102A, and 87 did not completely disintegrate for any temperature. Any increase in the calcium oxide over this minimum amount for any given clay does not increase the temperature of maximum disintegration.

Experiment	92	93	94
Temperature.....	1415°	1431°	1431°

The temperature of maximum disintegration is lowered by increasing the time of passage through the furnace.

Experiment	92	92A	94	94A
Temperature	1415°	1383°	1431°	1383°

When the ratio of CaO to $SiO_2 + Al_2O_3$ is enough for complete disintegration the addition of MgO does not change the temperature of maximum disintegration.

Experiment	92A	95A	94A	96A
Temperature	1383°	1383°	1383°	1389°

The substitution of R_2O_3 for SiO_2 materially raises the temperature of maximum disintegration.

Experiment	87	92	88	93	98	94
Temperature.....	1389°	1415°	1363°	1431°	1353°	1431°

For a given clay the amount of water required for normal consistency increases with increase of CaO provided the time of passage through the furnace is kept constant.

Experiment.....	92	93	94	92A	94A
Per cent. water.....	24	32	40	27	34

TEMPERATURE FOR FIRST PERFECT HOT TEST.

For a given clay the burning temperature necessary to obtain a perfect hot test increases with increase of CaO.

Experiment.	103	98	87	88	92	93	101	94	99
Temperature	1467°	1545°	1467°	1533°	1438°	1503°	1511°	1549°	1593°

This temperature is lowered by increase of time of passage through the furnace.

Experiment.....	92	92A	94	94A
Temperature.....	1438°	1431°	1549°	1478°

When the ratio of CaO to $SiO_2 + Al_2O_3$ is enough to ensure a perfect boiling test at some temperature, the addition of MgO does not materially raise the temperature necessary to obtain clinker giving a perfect boiling test.

Experiment.....	92A[1]	95A	94A	96A
Temperature.....	1431°	1455°	1478°	1487°

The substitution of R_2O_3 for SiO_2 lowers the temperature for a perfect pat when the ratio of CaO to acidic oxides is low.

Experiment	87	92	88	93
Temperature.....	1467°	1438°	1533°	1503°

With increasing amount of calcium oxide the temperature for perfect hot test is increased and the point is soon reached when a perfect hot test cannot be obtained at all.

Experiment	98	94	99	100
Temperature.....	1545°	1549°	1593°	none

The amount of water required for normal consistency varies within slight limits but does not rise over 25 per cent. irrespective of the clay used and the composition of cement.

OVERBURNING TEMPERATURE.

For a given clay the overburning temperature increases with increase of CaO.

Experiment.....	103	98	87	88
Temperature	1549°	above 1653°	1491°	1553°

Experiment ...	92	93	101	94	99	100
Temperature...	1438°	1503°	1557°	1573°	1613°	1625°

The overburning temperature is lowered by increasing the time of passage through the furnace.

Experiment.....	92	92A	94	94A
Temperature	1438°	1431°	1573°	1545°

MgO may replace CaO molecularly up to an empirical formula, $2RO.SiO_2, 2RO.Al_2O_3, 2RO.Fe_2O_3$, without much change in overburning temperature.

Experiment.....	102A	92A
Temperature.....	1445°	1431°

[1] his pat was free from cracks but rather weak.

When the CaO is at least $2CaO.SiO_2$,$2CaO.Al_2O_3$,$2CaO.Fe_2O_3$, the addition of magnesium oxide raises the overburning temperature only slightly, not nearly so much as an equivalent amount of calcium oxide.

Experiment 92A, 1431°; Experiment 95A, 1455°. These have same ratio CaO to acidic oxides, but 95A has increased MgO.

Experiment 95A, 1455°; Experiment 94A, 1545°. These have same ratio RO to acidic oxides, but in 94A the RO is nearly all CaO.

Experiment 94A, 1545°; Experiment 96A, 1557°. These have same ratio CaO to acidic oxides but 96A has increased MgO.

Experiment 102A, 1445°; Experiment 96A, 1537°; Experiment 100, 1625°. These have same ratio RO to acidic oxides but 102A overburns at almost same temperature as 92A, 96A at almost same temperature as 94A which has same ratio CaO to acidic oxides, while 100 which has almost all CaO has highest overburning temperature of any.

The substitution of R_2O_3 for SiO_2, molecule for molecule, materially lowers the overburning temperature.

Experiment ..	87	92	88	93	98	94
Temperature..	1491°	1438°	1553°	1503°	above 1653°	1573°

The water required for normal consistency with overburned cements is only slightly less than that required for cements burned to give perfect boiling test.

SUMMARY.

Viewed from the standpoint of the influence of chemical composition upon the changes in temperature necessary to produce a sound cement and the temperature at which the clinker will give trouble by sticking in the rotary, we find that:

The minimum temperature necessary to produce Portland cement which will give a perfect pat test *from fresh clinker* is about 1450° C. This temperature is for a minimum amount of calcium oxide. It increases with increase of calcium oxide until in ordinary commercial cements it reaches 1550°. With the most heavily limed commercial cements this figure would be somewhat higher. It depends somewhat on the length of time required to pass through the rotary, slow driving tending to lower the temperature. The substitution of Al_2O_3, or Fe_2O_3 for SiO_2, that is, the

use of a richer clay, lowers the overburning temperature but may *lower or raise* the temperature required for perfect boiling test. With mixtures low in calcium oxide, the burning temperature for perfect boiling test is lowered by this substitution, but with mixtures high in calcium oxide the burning temperature required for perfect boiling test is raised and may become coincident with the overburning temperature. Any attempt to raise the overburning temperature by increasing the proportion of lime will fail to give a perfect hot test even at the overburning temperature, as illustrated in Experiment 100. This is a confirmation of what manufacturing experience has shown—that with lean clays heavily limed there is a wide margin between the proper clinkering temperature and the overburning temperature, while with rich clays in order to prevent the clinker from balling-up, great care must be exercised to maintain the proper clinkering temperature. With the amount of calcium oxide found in ordinary cement the introduction of 8 or 9 per cent. of magnesium oxide has but little influence on the temperature for perfect boiling test or overburning temperature. So far as the clinkering is concerned, magnesia, as has been maintained by Newberry, acts as an inert substance.

While the conclusions above set forth seem to be fully warranted by our experiments, we realize that a much greater amount of experimental research must be performed, before the exact influence of each factor influencing the clinkering of cement can be determined with certainty. In the light of the knowledge gained by the present set of experiments, we are planning a much more complete series upon which we hope to report at some future date. In this new series we intend to include more cements whose basicity shall be equal to or greater than that found in the commercial cements. We have excluded from the present paper any discussion of phenomena connected with the setting of cement and its subsequent behavior aside from the amount of water required for normal consistency and the behavior under the boiling test. We have been studying this subject also for the past three years and hope later to present some results.

ANN ARBOR, MICHIGAN,
June, 1902.

ON THE QUANTITATIVE SEPARATION OF MALTOSE AND LACTOSE.

By Charles L. Boyden.

Received June 30, 1908.

The writer, in the course of a study on the composition of sundry infant and invalid foods now on the market, undertaken to fulfil a thesis requirement for graduation from the agricultural department of the University of Vermont, found it necessary quantitatively to separate maltose and lactose. He was unable to find, either in the literature or through correspondence with several chemists well informed in food analysis, any satisfactory method to this end. Such a separation may be accomplished, however, by the use of a certain variety of yeast, *Saccharomyces anomolus*, which removes maltose completely without acting on the lactose.

It is well understood that the two bisaccharides, maltose and lactose, need to be hydrolyzed before they may be fermented, and that the former yields two molecules of glucose and the latter, one of glucose and one of galactose as a result of hydrolysis. Glucose is then easily fermented. Yeasts usually contain hydrolytic enzymes, which are capable of changing maltose to a greater or less extent, but which are inactive with lactose.

In the course of the work carried out by the writer nine different species of yeasts were used. Eight of the yeasts were obtained from Kral, and one was a pure culture from ordinary Fleischmann's bread yeast. The yeasts from Kral's laboratory were: *Saccharomyces anomolus* Hansen, *S. cerevisiae I* Hansen, *S. cerevisiae Carlsberg unterhefe I* Hansen, *S. ellipsoideus I* Hansen, *S. farinosus* Lindner, *S. Kephir* Beijerinck, *S. Marxianus* Hansen, *S. Pastorianus I* Hansen. Pure cultures of each were grown in agar, from which they were transferred to Pasteur's fluid (Strassburger and Hillhouse's formula). Samples of commercial maltose (66.36 per cent. maltose, remainder mostly dextrin) and lactose of known composition were used separately, as well as in mixtures of definite strengths.

From 25 to 100 cc. of a solution of these sugars, usually 0.50 per cent. strong and containing 1 per cent. of Pasteur's mixture (Strassburger and Hillhouse), were heated at 100° C. in a steam sterilizer for thirty minutes on three successive days. The ster-

ilized fluid was then inoculated with the particular yeast under trial and incubated at 30° C. for from two to thirty days; then again sterilized at 100° C., cooled, made up to volume, filtered, and the sugar present determined by Allihn's method. The usual precautions to prevent contamination with organisms other than the yeast under trial were observed throughout the operation from inoculation to filtration. The temperature of 30° C. was chosen, inasmuch as bread yeast appeared to act most vigorously at this temperature. The percentages of maltose removed and of lactose remaining were readily calculated from the copper reduced prior to, and that reduced subsequent to, the removal of maltose. Obviously, when working with known quantities, the completeness or the incompleteness of the removal of the maltose may be readily measured in this manner.

From about 10 per cent. to nearly all of the maltose remained unacted upon by eight of the yeasts. One of these yeasts, however, after a few preliminary trials completely and uniformly hydrolyzed and fermented the maltose.

S. anomolus was much the most active yeast used. It produced a heavy white growth in tube cultures in a few days. After two days' inoculation at least three-fourths of the maltose had disappeared and the proportion of maltose modified uniformly decreased up to sixteen days, after which there was no apparent change. It was found necessary to filter through a bacterial filter in order to remove the yeast cells and to prevent a precipitation of the flocculent matter by the Allihn solution, which was equivalent to a weight of from 1 to 2 per cent. of copper. The following table shows the result of some of the work with this yeast. The figures clearly show the relation of filtration, of tne time element and of the use of the Pasteur's mixture to complete success.

Maltose taken. Gram.	Pasteur's mixture. Grams.	Volume of solution.	Solution. inoculated. cc.	Days acted on.	CuO from 25 cc. solution.	Maltose remaining. Per cent.
1	2	200	50	2	0.0138	7.47[1]
1	2	200	50	4	0.0044	2.38[1]
1	2	200	50	13	0.0030	1.63[1]
1	2	200	50	16	0.0025	1.35[1]
1	2	200	50	16	0.0000	none[2]
1	none	200	50	11	0.0198	10.68[1]
1	none	200	50	34	0.0089	4.82[2]
1	0.5	200	50	31	0.0040	2.16[2]
1	1	200	50	14	0.0063	3.42[2]
1	1	200	50	38	0.0000	none[2]

[1] Not filtered with bacterial filter. [2] Filtered with bacterial filter.

It may be remarked that when this yeast was grown for from four to twenty-four days in a solution of lactose, from 98 to 100.96 per cent. lactose was recovered, showing that this sugar was unaltered by the yeast. It may also be remarked that the fermentation method, using *S. anomolus*, has been tried upon several of the proprietary foods upon the market; that through the courtesy of the chemist of one of the companies manufacturing this class of goods the writer has been allowed to compare analytical results with manufacturer's formulas as regards percentages of maltose and lactose; and that a reasonably close agreement has been found.

It is interesting to note that in those solutions in which the other yeasts failed—as they always did—completely to transform all the maltose, reinoculation with *S. anomolus* readily hydrolyzed and removed the remaining maltose, while in no case did it appear in any way to affect their lactose content.

Vigorous growth is needed to hydrolyze the last traces of maltose. To produce this vigorous growth it is necessary to add some of the mineral elements found in the ash of yeast. Pasteur's mixture (Strassburger and Hillhouse) furnishes the necessary elements.

The method in its present form may be briefly outlined as follows: The solution containing maltose and lactose having been made approximately 0.5 per cent., and containing 1 per cent. of Pasteur's mixture, 50 cc. are heated for three successive days in a steam sterilizer, under the usual precautions, to 100° C. for thirty minutes. The fluid thus sterilized is inoculated liberally with a pure culture of *S. anomolus* and incubated at about 30° for from two to three weeks, the culture having been grown in agar and transferred to Pasteur's fluid prior to its use. After the incubation, the fluid is filtered through a bacterial filter and the copper determined in the usual manner by Allihn's method. The difference between the copper thus determined and that present prior to inoculation may be calculated as maltose, the remainder as lactose.

The writer is under obligation to Professor L. R. Jones, botanist and Mr. C. H. Jones, chemist of the Vermont Station for helpful advice and suggestion.

CHEMICAL LABORATORY, VT. AGR. EXP. STATION,
UNIV. OF VT., BURLINGTON, VT.

ON THE ELECTRICAL CONDUCTIVITY OF URINE IN RELATION TO ITS CHEMICAL COMPOSITION.[1]

By J. H. Long.

Received July 30, 1902.

Among the newer applications of the methods of modern physical chemistry some of the most important are certainly those employed in the solution of problems in physiology and physiological chemistry. At first sight one of the least promising of these methods is that of the determination of electrical conductivity as applied to the fluids of the body, but the labors of Roth,[2] Stewart,[3] Bugarszky and Tangl,[4] and others have shown the possibilities of the method in the examination of blood serum. In respect to inorganic constituents blood serum is much more constant than is urine, and the variations in the conductivity of the latter appear at first sight so irregular as to be beyond simple formulation. This notion, however, is not quite correct. It has been shown by Bugarszky[5] that certain general relations are easily observed, and among others the connection between the total ash and the conductivity.

It must be remembered that the conductivity of the urine is practically due to the mineral salts present only. The most abundant of all the urinary constituents, the urea, is so near a non-conductor in solution that its effect may be safely neglected. Even the low value given by Trübsbach[6] is probably high, as shown by some of my own observations with carefully prepared urea. The creatinin, ammonia, xanthin bodies, uric acid and urates have all but a slight conductivity and their effect in lowering the conductivity of the mineral salts is extremely small. For investigations of this kind it is exceedingly difficult to obtain urea pure enough to be used as a standard. Nearly all found in the market contains notable quantities of potassium sulphate, sometimes several per cent., and purification by crystallization from alcohol is attended by great loss. Besides this, in using hot solu-

[1] Read by title at the Pittsburg meeting of the American Chemical Society, July 2, 1902.

[2] *Centralblatt für Physiologie*, 11, 271 (1897).

[3] *Ibid.*, 11, 332 (1897).

[4] *Ibid.*, 11, 297 and 301 (1897).

[5] *Pflüger's Archiv für die gesammte Physiologie*, 68, 389 (1897).

[6] *Ztschr. phys. Chem.*, 16, 708; also in Kohlrausch und Holborn's "Leitvermögen der Elektrolyte," p. 184.

tions in strongest alcohol some of the urea is always converted into ethyl urethane, with further loss on crystallization. Unless, therefore, the urea is very carefully purified its effect on the conductivity may appear sensibly positive instead of negative.

In view of these facts it follows that the conductivity of the urine is a function of the total mineral content and the determination has a value somewhat analogous to that of the specific gravity; but it is much more definite, however, and as the degree of accuracy possible is high the method must certainly prove of value in studies of the metabolism of inorganic substances. To bring out these points I have undertaken recently a number of experiments. In the first of these I have determined the volume, specific gravity, electrical conductivity, chlorine and urea in the urine of two individuals, collected at regular intervals through three days. These results are shown in Tables I and II. The specific gravity was found by the Westphal balance, adjusted for a temperature of 20°. The figures given are referred to water at 4°. The accuracy of the readings was controlled by pycnometer determinations on several samples. The conductivity was found at 20°, always, the temperature being sharply maintained within 0.1°, by the Kohlrausch method, using a U-tube with a resistance capacity, $C = 8.415$. The resistance measurements were made with a large Kohlrausch-Wheatstone bridge, the wire corrections being known, and the values of the 100 and 1000 ohm comparison resistances, also. The urine resistance, R, measured varied between about 250 and 800 ohms, from which the conductivity, K, was found by the formula:

$$K = \frac{C}{R}$$

For an observed resistance of 500 ohms K is therefore 0.016830.

The chlorine was found by the usual Volhard-Arnold process, the liquid being filtered before titration of the excess of silver by the thiocyanate. In the urea titration I used the Liebig process, employing the approximate corrections described by me.[1] The corrections actually used were based on previous experiments with the urine of the same individuals. In the tables the reduced and corrected values only are given, and the chlorine is calculated as sodium chloride. For the purpose in view this is admissible, and

[1] This Journal, 22, 632.

INDIVIDUAL A.

1. Period.	2. Volume passed. c.c.	3. Specific gravity at $\frac{30°}{4°}$.	4. Conductivity, κ.	5. Chlorine as sodium chloride. Grams per 100 cc.	6. Urea. Grams per 100 cc.	7. Specific gravity—amount due to urea, etc.	8. Excess of specific gravity over that of water, due to mineral substances.	9. Fraction of conductivity not due to sodium chloride.	10. Ratio of conductivity to sodium chloride.
Observations of first day: Excretion = 1162 cc. Liquid consumption = 1750 cc.									
6–9 A.M.	145	1.024	0.02589	1.316	2.95	1.015	0.017	0.00590	
9–12	178	1.023	0.03021	1.579	2.55	1.015	0.017	0.00632	
12–3	135	1.024	0.02834	1.416	2.60	1.016	0.018	0.00692	
3–6	118	1.027	0.02790	1.292	3.31	1.017	0.019	0.00827	
6–9 P.M.	128	1.026	0.02694	1.275	2.89	0.017	0.019	0.00757	
9–6	458	1.023	0.02421	1.170	2.82	1.015	0.017	0.00644	
MEANS, 3-hour period :		1.024	0.02650	1.298	2.84	1.016	0.018	0.00679	0.0204
Observations of second day: Excretion = 1365 cc. Liquid consumption = 2100 cc.									
6–9 A.M.	192	1.020	0.02645	1.427	2.51	1.012	0.014	0.00486	
9–12	245	1.020	0.02926	1.608	1.87	1.014	0.016	0.00491	
12–3	155	1.026	0.02803	1.345	2.65	1.018	0.020	0.00768	
3–6	113	1.026	0.02702	1.211	3.10	1.017	0.019	0.00862	
6–9 P.M.	155	1.025	0.02702	1.298	2.80	1.017	0.019	0.00730	
9–6	405	1.025	0.02122	0.848	3.45	1.015	0.017	0.00772	
MEANS, 3-hour period :		1.024	0.02518	1.179	2.91	1.015	0.017	0.00707	0.0214
Observations of third day: Excretion = 1324 cc. Liquid consumption = 1870 cc.									
6–9 A.M.	230	1.022	0.02683	1.433	2.47	1.015	0.017	0.00515	
9–12	260	1.021	0.02939	1.602	2.18	1.015	0.017	0.00516	
12–3	160	1.026	0.02793	1.428	2.77	1.018	0.020	0.00633	
3–6	134	1.026	0.02755	1.345	2.99	1.017	0.019	0.00712	
6–9 P.M.	146	1.025	0.02580	1.165	2.82	1.017	0.019	0.00810	
9–6	394	1.023	0.01997	0.731	3.21	1.013	0.015	0.00833	
MEANS, 3-hour period :		1.024	0.02468	1.146	2.86	1.015	0.017	0.00710	0.0215

INDIVIDUAL B.

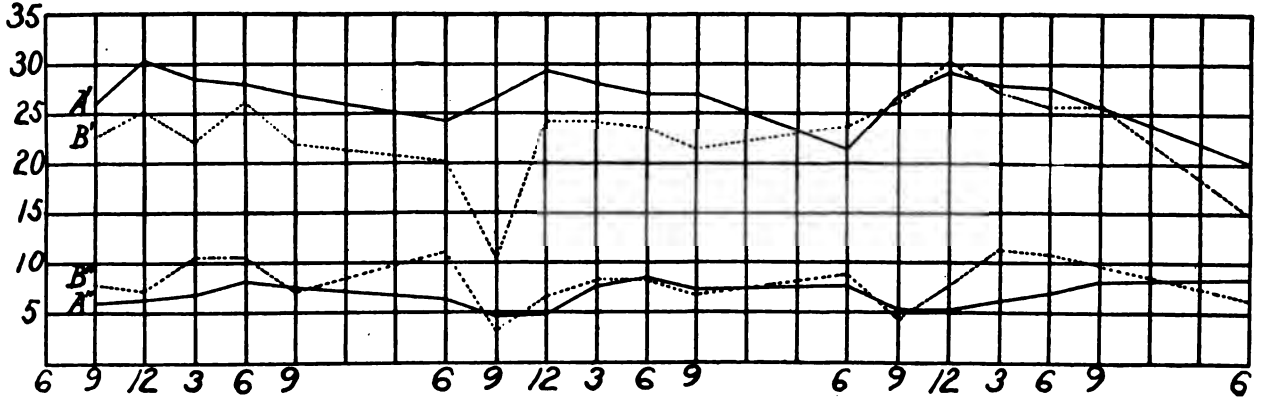
1. Period.	2. Volume passed. cc.	3. Specific Gravity at $\frac{15}{15}$°	4. Conductivity, κ.	5. Chlorine as sodium chloride. Grams per 100 cc.	6. Urea. Grams per 100 cc.	7. Specific Gravity—amount due to urea, etc.	8. Excess of specific gravity over that of water due to mineral substances.	9. Fraction of conductivity not due to sodium chloride.	10. Ratio of conductivity to sodium chloride.
Observations of first day: Excretion = 861 cc. Liquid consumption = 1815 cc.									
6–9 A.M.	112	1.022	0.02264	0.948	2.35	1.015	0.017	0.00779	
9–12	220	1.019	0.02519	1.182	1.54	1.014	0.016	0.00723	
12–3	77	1.026	0.02226	0.737	3.20	1.016	0.018	0.01052	
3–6	70	1.027	0.02614	0.994	3.52	1.016	0.018	0.01056	
6–9 P.M.	198	1.021	0.02178	0.936	2.49	1.013	0.015	0.00701	
9–12	184	1.026	0.02008	0.562	3.85	1.014	0.016	0.01099	
MEANS, 3-hour period :		1.024	0.02228	0.810	3.08	1.014	0.016	0.00951	0.0275
Observations of second day: Excretion = 1331 cc. Liquid consumption = 2565 cc.									
6–9 A.M.	410	1.007	0.01039	0.456	1.10	1.004	0.006	0.00301	
9–12	122	1.017	0.02408	1.119	2.36	1.010	0.012	0.00655	
12–3	96	1.023	0.02422	0.998	2.99	1.014	0.016	0.00864	
3–6	138	1.024	0.02355	0.971	3.11	1.015	0.017	0.00833	
6–9 P.M.	180	1.021	0.02144	0.936	2.58	1.013	0.015	0.00678	
9–6	285	1.024	0.02369	0.942	3.11	1.015	0.017	0.00893	
MEANS, 3-hour period :		1.020	0.02184	0.913	2.70	1.013	0.015	0.00751	0.0239
Observations of third day: Excretion = 1099 cc. Liquid consumption = 1390 cc.									
6–9 A.M.	278	1.015	0.02629	1.439	0.93	1.012	0.014	0.00453	
9–12	158	1.022	0.03037	1.491	1.46	1.018	0.020	0.00782	
12–3	92	1.029	0.02720	1.006	3.19	1.020	0.022	0.01143	
3–6	71	1.030	0.02566	0.948	3.48	1.020	0.022	0.01081	
6–9 P.M.	112	1.027	0.02577	1.023	3.24	1.017	0.019	0.00974	
9–6	388	1.014	0.01492	0.527	1.74	1.009	0.011	0.00639	
MEANS, 3-hour period :		1.021	0.02251	0.936	2.19	1.014	0.016	0.00794	0.0240

besides is perfectly correct as far as the urines of Table I are concerned. For the urines of Table II, individual B, no previous determination of the relation of sodium to potassium had been made.

A consideration of the tables discloses several interesting facts. In both sets the specific gravities appear low for the amounts of urea and salt present, but it must be remembered that they are based on the temperature of 20° referred to water at 4°. The means given for each day are calculated on the assumption that the collections made from 9 P.M. to 6 A.M. represent three 3-hour periods. The mean specific gravities for individual A are constant and the conductivities nearly so. There is no simple relation between the two classes of data. Nor is any relation seen when we subtract from the observed (corrected) specific gravity that fraction due to the urea present. This appears in column 7. To obtain these figures I found the specific gravity of several urea solutions and deduced this mean value; 1 gram of urea in 100 cc. adds 0.0027 to the specific gravity of water or a weak salt solution. For each gram of urea found per 100 cc. I have applied the correction 0.003 to include the effect of the other organic bodies. In column 8 I have given the excess of the specific gravity due to mineral substances over that of water at the standard temperature; *viz.*, 0.9983. The variations here are so slight as to have no practical significance; but in columns 9 and 10 we have numbers which are characteristic and definite enough to afford certain indications. From well-determined values, those found in the tables of Kohlrausch and Holborn, for example, it is possible to calculate the conductivities of weak salt solutions, such as those concerned here. From the total observed conductivity I have taken out the fraction due to the sodium chloride found to be present, and have put down the remaining values in column 9. These numbers represent the conductivities due to salts other than the sodium chloride of the food, and are therefore a measure of the mineral products of metabolism present. We have here mainly the sulphates and phosphates of oxidation and it will be seen that the mean values are pretty constant for individual A, through the three days. For B the results are somewhat less constant but distinctly different from those for A. The fraction of the conductivity due to meta-

bolic products is much greater for B than for A in the mean, and at several periods reaches an amount which is nearly one-half the total. In both cases the chlorine excretion is greatest during the morning hours, while the conductivity due to other salts reaches a maximum later. It will be noticed that these numbers which are given in column 9 bear no close relation to the specific gravity numbers given in columns 3, 7 and 8. The relation of the conductivity to the salt excretion is given in columns 10, and for A is practically constant. For B the ratio is a different one, but not quite a constant. Inasmuch as salt is the chief mineral substance excreted a relation of this kind is a practical necessity. The curves in the adjoining figure show the variations in the total conductivity from period to period, and also the variations in the fraction of the conductivity not due to sodium chloride.

To further show the relation of composition to conductivity a number of complete analyses have been made of mixed normal urines. The conductivities of these urines were found and also the conductivities of artificial mixtures made up from the results of analyses. The analyses are given in the tables. Numbers 1, 2 and 3 are of urines from men consuming a mixed animal and vegetable diet. The results were obtained in April while the weather was cool and the excretion normal. Numbers 4, 5 and 6 are from the urine of vegetarians consuming the mixed nut, vegetable and cereal foods used by the authorities of the Battle Creek Sanitarium. Each urine represented the total day's excretion of three or four individuals, and aside from the special purpose here in view the analyses have considerable scientific value because very few complete examinations are found in the literature. The average excretion for each individual contributing to Nos. 1, 2 and 3 was about 1200 cc., while for the individuals furnishing the urines 4, 5 and 6 the average excretion was about 1000 cc. These results were obtained later, in the warm weather of June.



Explanation of the curves: Curve A' represents the conductivity of the urine from individual A through the three days. A'' shows the variations in the conductivity due to other salts than chlorides for the same period. B' represents the results of the examination for total conductivity for individual B, and B'' finally, the conductivity not due to sodium chloride. The abscissa spaces represent 3-hour periods. The ordinate spaces correspond each to $K = 0.005$. In the curve A' three distinct maxima are easily seen which correspond closely to minima in A''. The variations in B' and B'' seem to follow a somewhat different order.

TABLE OF COMPLETE URINE ANALYSES.

Nos. 1, 2 and 3 mixed diet.
Nos. 4, 5 and 6 vegetarian.
Results in grams per 100 cc.

	1.	2	3.	4.	5.	6.
Specific gravity $\frac{20°}{4°}$	1.024	1.020	1.026	1.017	1.028	1.021
Conductivity, K	0.02372	0.02402	0.02793	0.01984	0.02898	0.02251
Potassium, K	0.1980	0.2455	0.2604	0.1416	0.4872	0.3869
Sodium, Na	0.3820	0.3710	0.4647	0.3419	0.3578	0.2705
Calcium, Ca	0.0104	0.0086	0.0132	0.0031	0.0164	0.0130
Magnesium, Mg	0.0092	0.0121	0.0152	0.0144	0.0225	0.0341
Ammonium, NH_4	0.0900	0.0840	0.1080	0.0800	0.0745	0.0576
Chlorine, Cl	0.7366	0.7160	0.7739	0.5254	0.8165	0.5893
Phosphoric acid, PO_4 ..	0.1143	0.1742	0.3135	0.2062	0.3111	0.2230
Sulphuric acid, SO_4 ...	0.1640	0.1964	0.3230	0.1965	0.2790	0.2039
Urea, CON_2H_4	2.85	2.60	2.97	2.11	2.95	2.80
Uric acid, $(C_5H_2N_4O_3)''$	0.0641	0.0691	0.0876	0.0549	0.0769	0.0838
Creatinin, $C_4H_7N_3O$...	0.1750	0.1790	0.1414	0.0252	0.0910	0.1050

Some of these results are very interesting but a discussion of peculiarities revealed will be left for another occasion. An attempt was next made to duplicate the urines as nearly as possible by mixing salts, urea and creatinin in certain proportions. It is not possible in any case to obtain a perfectly clear artificial mixture containing all the bases and acids in the proportions found, but mixtures were made by combining the phosphoric acid and the whole of the calcium and magnesium first. The acid phosphate solutions obtained were clear, and strongly acid to litmus. Then the salts were added in amounts shown in the table, the urea and the creatinin also. The uric acid and a part of the ammonium were temporarily left out. In each case 250 cc. of mixture was made, and the conductivity found.

DUPLICATION OF ANALYSES.

Results in grams per 100 cc.

Substances taken.	1.	2.	3.	4.	5	6.
NaCl	0.9716	0.9436	1.1819	0.8686	0.9100	0.6880
KCl	0.3089	0.3013	0.1191		0.5554	0.3610
K_2SO_4	0.0804	0.1951	0.4411	0.3154	0.4363	0.3704
$(NH_4)_2SO_4$	0.1646	0.1222	0.1098	0.0312	0.0527	
$CaCO_3$	0.0260	0.0215	0.0330	0.0078	0.0410	0.0325
MgO	0.0153	0.0202	0.0250	0.0240	0.0375	0.0568
K_2						0.0312
PO_4	0.1143	0.1742	0.3135	0.2062	0.3111	0.2230
CON_2H_4	2.85	2.60	2.97	2.11	2.95	2.80
$C_4H_7N_3O$	0.175	0.179	0.1414	0.0252	0.0910	0.105
Conductivity found ...	0.02264	0.02291	0.02628	0.01910	0.02843	0.02059

After finding the conductivity of the clear solutions, the ammonia lacking and the uric acid were added, the ammonia from a strong standard solution. The mixtures were shaken and allowed to

settle some hours, when the conductivities were again found. A slight correction in the results was made on account of the trifling dilution on adding the ammonia. The results were as follows, from the solutions now neutral to litmus paper:

	1.	2.	3.	4.	5.	6.
Remaining NH_4 added.....	0.0451	0.0507	0.0731	0.0715	0.0599	0.0576
Uric acid ($C_5H_4N_4O_3$) added	0.0641	0.0691	0.0876	0.0549	0.0769	0.0838
New conductivity at 20°....	0.02332	0.02400	0.02768	0.01944	0.02886	0.02158

It is interesting to note that the new conductivities correspond very nearly with those found for the original urines. The values found before the addition of the uric acid and the ammonia were all sensibly lower, as might be expected, but with the final additions higher conductivity is secured, notwithstanding the fact of the formation of a slight precipitate. The fraction of the conductivity due to the free uric acid or to the urates is small as the investigations of His and Paul[1] would suggest. These results are in a measure a check on the general accuracy of the analyses.

Certain general conclusions may be drawn from these experiments:

1. The electrical conductivity of the urine varies essentially with the amount of inorganic salts present and taken alone is a datum of relatively little importance because of the effect of the large amount of sodium chloride present; but,

2. After deducting the fraction of the conductivity due to the sodium chloride content a remainder is left which has importance in indicating the extent of certain metabolic changes. The amounts of sodium chloride and other salts and the corresponding conductivities are shown in a manner easy for comparison in the tables of complete analyses and duplications.

3. Inasmuch as the conductivity may be readily and accurately determined the variations in the value of this residual conductivity are of importance in fixing the lag in the rate of inorganic excretion.

4. For the purpose of making other comparisons it may be necessary to determine the conductivity in diluted urine, where the salts act with their maximum capacity. Some work of this kind is in progress.

NORTHWESTERN UNIVERSITY, CHICAGO,
June, 1902.

[1] *Ztschr. physiol. Chem.*, 31, 1.

THE RETENTION OF ARSENIC BY IRON IN THE MARSH-BERZELIUS METHOD.[1]

By Charles Lathrop Parsons and Morris A. Stewart.

Received July 2, 1902.

An extended discussion of the determination of arsenic in small quantities has recently been published in the English chemical journals and several chemists have called attention to the fact that different samples of zinc produce mirrors of varying intensity from like amounts of arsenic.

The Joint Committee of the Society of Chemical Industry and the Society of Public Analysts in reporting the details to be followed in carrying out the Marsh-Berzelius method state that "It is important to note that some pure zinc is, from a cause at present unknown, not sufficiently sensitive; that is to say, the addition of minute quantities of arsenic produces no mirror."[2] O. Hehner[3] states that he found some zinc which, while retaining the arsenic in the form of rods, did not do so when granulated, and further claims that the addition of platinic chloride renders the reaction less delicate. Again[4] the same author finds that minute quantities of arsine are not evolved when aluminum and sodium hydroxide are used as a source of the hydrogen, and that even so much as 0.2 mg. in 25 cc. of solution gives no mirror. Wöhler as far back as 1839 stated that when arsenical pig iron is dissolved in dilute sulphuric acid the arsenic does not pass off with the hydrogen but remains as a salt of arsenic acid.[5] Headden and Sadler[6] found that very low results for arsenic were obtained by the Marsh-Berzelius method on arsenopyrite, FeAsS. The amounts were increased by removing the iron, and they suggest that, as much better results were obtained on duplicates from the same bar of zinc, one-half being used in each, the difficulty might be due to the carbon present. They later state[7] that the addition of copper sulphate or platinic chloride also made the results much lower.

[1] Read at the Pittsburg meeting of the American Chemical Society.
[2] *J. Soc. Chem. Ind.*, 21, 95 (1902).
[3] *Ibid.*, 20, 194.
[4] *Ibid.*, 20, 200.
[5] *Ann. der Pharm.*, 31, 95 (1839).
[6] *Am. Chem. J.*, 7, 341.
[7] *Ibid.*, p. 342.

Sautermeyer[1] found that even when 0.1 gram of arsenic trioxide was purposely added he could get no reaction for arsenic when 1 gram of iron was dissolved in dilute hydrochloric acid in a Marsh apparatus and the flame allowed to play on porcelain. The test works, however, when 2.5 grams of zinc are added to the iron. Under these conditions 1 mg. of arsenic may be detected although it comes off slowly. No quantitative determinations were made.

Although the results obtained by the before-mentioned authors would seem to indicate that the presence of iron was highly deleterious the fact seems to have been entirely lost sight of by chemists and in most instances the investigators themselves attribute their low results to other causes or, at least, do not state the necessity for the absence of iron. In fact the contrary is frequently true and recommendations to add ferric chloride to insure regularity of flow of gas will often be found in the literature, even so well known an authority as Mr. A. H. Allen[2] recommending that the zinc always contain, at least, a trace of iron to insure the regular evolution of hydrogen and the formation of uniformly deposited brown mirrors. This condition will probably almost always exist, as our experience has been that it is almost impossible to purchase zinc free from iron.

Our attention was called to the fact that the Marsh-Berzelius method often fails to give up, as arsine, all the arsenic present, by repeated failures to obtain in the form of mirrors the weight of arsenic which had been added to the generator, while a careful examination of the gas that had passed through the heated tube proved it to be arsenic-free. The remaining arsenic, therefore, could be in the generator only. To overcome the difficulty we used the zinc in rod form and then the same zinc granulated, zinc containing carbon and zinc carbon free, but found they all retained arsenic. We also tried many samples of zinc, but while different percentages of the arsenic present were recovered we were not able to obtain any sample of zinc that yielded all the arsenic that had been added.

In order to investigate the question, relatively large amounts of zinc were used and varying amounts of arsenic added. We soon found that if a too large amount of arsenic, relative to the escaping

[1] *Chem. Ztg.*, **18**, 1021.
[2] *J. Soc. Chem. Ind.*, **21**, 94 (1902).

hydrogen was present, as arsenious acid, it was reduced first to the metallic and not to the gaseous state. This is probably so well known that the fact is seldom mentioned, but it was at the time new to us. By never using more than a few centigrams of arsenic trioxide this difficulty was avoided and the residues left in the generator, which with some samples of zinc were voluminous, were arsenic-free or so nearly so as to yield but a faint brown coloration in place of a mirror. These residues consisted generally of lead and carbon but as we could trace no relation between their presence and the retentive action of the zinc there will be no need to mention them further. The retained arsenic was, therefore, in the solution.

The solution left in the generator was filtered, acidified with strong nitric acid to prevent volatilization of arsenious chloride, if present, and was evaporated to hard dryness over a free flame. As the last of the water passed off a brick-red precipitate, intermixed with the zinc chloride, was formed, which was insoluble in water and strong nitric acid. The zinc chloride, together with any lead chloride, was dissolved out with hot water and was now found to be iron-free and to still yield no further mirror of arsenic. In fact, subsequent trials showed this to be a most excellent method of preparing pure zinc chloride free from iron, as the iron was quite perfectly separated even when considerable quantities had been added. The brick-red precipitate, on being dissolved in concentrated hydrochloric acid and again treated in the Marsh apparatus, yielded a large part of the arsenic which had been retained, as arsine, but again a portion was held back. By twice repeating the process of evaporation of the solution with nitric acid and re-treating the red precipitate formed, almost all of the arsenic added was recovered.

To determine the character of the red precipitate, a quantity was prepared, carefully washed and dried in a steam-bath. Washing was difficult, unless quickly done, as the precipitate had a decided tendency to become colloidal and it was found by no means as simple to free it from zinc as it had been to free the zinc chloride from iron. Samples were finally secured which were zinc-free. Several samples prepared in this manner were found to contain only iron, water and arsenic. No nitrogen was present. The material was therefore a hydrated iron oxide carrying arsenic.

Several attempts to determine in what form the arsenic was held have met with failure. The arsenic appears to be not an essential constituent of the red precipitate for it is present in very varying amounts and we have prepared an exactly similar compound arsenic free.

An analysis of two separate samples showed them to contain:

	Fe_2O_3	As
Sample 1	86.4	0.75
Sample 2	87.1	1.53

In both instances the arsenic was deposited as a mirror and weighed, as the quantity was so small compared to the iron that the ordinary gravimetric separation proved inadmissible. Accordingly the amounts are lower than the reality. A few of the actual experiments performed in this preliminary work will prove of interest.

(1) With no iron present but that contained in ordinary reagent "arsenic-free" zinc:

Arsenic-free, granulated zinc, containing iron, lead and carbon as impurities used and 0.05 gram of arsenic trioxide, in solution in hydrochloric acid were added. A considerable residue of lead and carbon remained, which, after being washed, dissolved in nitric acid, and re-treated in a Marsh apparatus, yielded a mere trace of arsenic. The solution evaporated to dryness with nitric acid, over free flame, gave a brick-red precipitate which, after being carefully washed, dried, dissolved in hydrochloric acid and re-treated in a Marsh generator yielded a mirror weighing 0.0025 gram. The zinc chloride and washings from the red precipitate were arsenic-free.

(2) With an excess of iron salt added:

Arsenic-free stick zinc was used. Several cubic centimeters of a concentrated solution of ferric chloride and 0.3 gram of arsenic trioxide was added in hydrochloric acid solution. Results as in (1) except that a large amount of the red precipitate was formed and a determination of a portion of it gave a mirror equivalent to 0.032 gram of arsenic in the whole.

(3) To find the proportion of arsenic recovered when the red precipitate is re-treated in a Marsh apparatus:

Arsenic-free zinc containing iron, hydrochloric acid, and 0.00506 gram of arsenic were used.

First mirror deposited 0.00425 gram; held back by iron 0.00081 gram.

The generator solution was evaporated with nitric acid, the red precipitate washed, dissolved in hydrochloric acid, and re-treated in the Marsh apparatus.

Second mirror deposited 0.00055 gram; held back by iron 0.00026 gram.

The generator solution was evaporated with nitric acid, the red precipitate washed, dissolved in hydrochloric acid, and re-treated in the Marsh apparatus.

Third mirror deposited 0.0001+ gram.

(4) To find if the same action took place when sulphuric acid was used instead of hydrochloric acid:

87 grams zinc, 25 grams ferrous sulphate in crystals, 0.5 gram arsenic trioxide, and dilute sulphuric acid were used. After the action ceased the sulphates were all precipitated by barium chloride, filtered, the solution treated with nitric acid and evaporated as before. The red precipitate formed easily and, being treated once in the Marsh generator, gave a mirror weighing 0.0054 gram.

In all of the experiments to follow, the method of Marsh-Berzelius, as outlined by the Joint Committee of the Society of Chemical Industry and the Society of Public Analysts[1] was used, care being taken to remove by lead acetate any hydrogen sulphide or selenide that might be present, as Rosenheim[2] and others have shown that selenium has a marked inhibitive action on the formation of mirrors. The mirrors were, however, weighed instead of being compared to standard mirrors as the nature of the investigation necessarily precluded their use, we being unable to procure any zinc that did not retain some arsenic. Many attempts were made to procure, on the market, iron-free zinc, but without success. The purest obtainable contained but 0.0011 per cent., which would ordinarily be considered as a mere trace. When looked at from the standpoint of the small amounts of arsenic determinable by the Marsh method it is, however, considerable. It may be well also to state here that our experience shows us that zinc in the so-called powdered form in which the grains are much the same size and approximately 1 mm. in

[1] *J. Soc. Chem. Ind.*, 21, 94 (1902).
[2] *Chem. News*, 83, 280.

diameter, is much the best form to use, as it gives a large surface for action and a corresponding uniformity in the flow of gas, which can be obtained from no other form.

Using the purest zinc obtainable, containing 0.0011 per cent. iron, no arsenic, and leaving no residue or but a mere trace, in the generator, when slight excess of acid was added, we next proceeded to determine the effect of adding known amounts of iron and of ferric chloride. Some 30 to 40 grams of zinc were used for each experiment. In order to obtain an alloy of iron and zinc we used the zinc in the rod form, added iron reduced by hydrogen, fused the whole and granulated. The alloying was fairly successful when small amounts of iron were used but was seldom complete with the larger quantities. Each sample made was proved to give no mirror itself before the addition of any arsenic.

A preliminary experiment on the purest (Fe 0.0011 per cent.) zinc gave results as follows: Arsenic taken, 0.0050 gram; arsenic found, first mirror, 0.0048 gram.

On evaporating with nitric acid and re-treating the small amount of red precipitate formed, a light brown mirror, too small to be weighed, but representing a small fraction of a milligram was obtained. This is especially noteworthy as showing that even with this small amount of iron some arsenic is retained.

EXPERIMENTS WITH ZINC ALLOYED WITH IRON.

The alloying was not always perfect, especially with the larger amount.

1. Alloy, 100 grams zinc; 0.2 gram iron: Arsenic taken, 0.0025 gram; first mirror, 0.0008 gram, 32 per cent.

2. Alloy, 100 grams zinc; 1 gram iron: Arsenic taken, 0.0050 gram; first mirror, 0.0017 gram, 34 per cent.

3. Alloy, 100 grams zinc; 5 grams iron: Arsenic taken, 0.0050 gram; first mirror, 0.0017 gram, 34 per cent.

4. Alloy, 100 grams zinc; 20 grams iron: Arsenic taken, 0.0050 gram; first mirror, 0.0025 gram, 50 per cent.

EXPERIMENTS TO SHOW THE EFFECT OF FERRIC CHLORIDE IN THE GENERATOR SOLUTION.

1. 30 grams purest zinc, with 0.2 per cent. iron as $FeCl_3$ added to generator: Arsenic taken, 0.0050 gram; first mirror, 0.00345 gram, 69 per cent.

2. 30 grams purest zinc, with 1 per cent. iron as $FeCl_3$ added to generator: Arsenic taken, 0.0050 gram; first mirror, 0.0027 gram, 54 per cent.

3. 30 grams purest zinc with 5 per cent. iron as $FeCl_3$ added to generator: Arsenic taken, 0.0050 gram; first mirror, 0.00295 gram, 59 per cent.

4. 30 grams purest zinc with 20 per cent. iron as $FeCl_3$ added to generator: Arsenic taken, 0.0050 gram; first mirror, 0.0016 gram, 32 per cent.

5. 30 grams purest zinc with 15 per cent. iron as $FeCl_3$ added to generator: Arsenic taken, 0.0001 gram; first mirror, less than 0.000001 gram.

From the results of our work we are forced to the conclusion that iron, whether as an alloy with the zinc or in the generator as a soluble salt, must be avoided, if exact quantitative results are desired. Whenever iron was present, even in small amounts, we have never failed to find arsenic in the red precipitate of hydrated iron oxide, formed by evaporating the liquid contents of the generator with nitric acid. This fact must give rise to serious error in the determination of very small amounts of arsenic by the use of standard mirrors, unless special precautions are taken, and it is for the determination of these small fractions of a milligram that the Marsh-Berzelius method finds its special application. Although our results do not show any definite amounts of arsenic retained by a given percentage of iron present as impurity we are inclined to believe that the amount retained would be fairly definite where the amount of iron present was very small. If this is true, the method of using standard mirrors, so universally adopted, will give results of essential accuracy, if the precaution be taken to always prepare the standards from the same zinc to be afterwards used in the analysis. It is also necessary that the zinc be as nearly free from iron as can possibly be obtained and that soluble salts of iron be kept out of the generator. It, accordingly, will be necessary in preparing solutions containing iron for analysis to reduce them and distil off the arsenic, as arsenious chloride, before adding to the generator. As a qualitative test we have never failed to get a mirror, even with iron present, when as much as 0.01 mg. of arsenic was added.

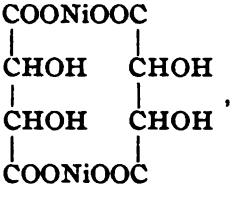
NEW HAMPSHIRE COLLEGE, DURHAM, N. H.,
June 1, 1902.

ON THE CONSTITUTION OF CERTAIN ORGANIC SALTS OF NICKEL AND COBALT AS THEY EXIST IN AQUEOUS SOLUTION.[1]

BY O. F. TOWER.

Received July 2, 1902.

IT has been shown in a former paper that the molecular conductivities of aqueous solutions of nickel and cobalt tartrates are exceptionally small, and furthermore that the apparent molecular weights derived from the freezing-point method considerably exceed the molecular weights calculated from the simple formulas of the salts.[2] It was suggested that these unusual results could be accounted for on the assumption of polymerization. The formula,



was given as expressing possibly the constitution of a molecule of nickel tartrate. Such a molecule would very likely be much less dissociated in solution than a simple molecule. In order to investigate this problem more fully these same methods have been applied to the tartrates of other metals and to the nickel, cobalt, and magnesium salts of certain other organic acids.

These salts were prepared from pure chemicals of standard make. The solutions were made by treating an excess of the carbonate or oxide of the metal with a sufficiently dilute solution of the acid. In a few instances the hydroxide of the metal was employed. On account of the slight solubility of most of these organic salts, the quantity of salt in solution after the acid had become neutralized was almost never equivalent to the quantity of acid taken, because some of the salt was precipitated while the action was going on. It was therefore necessary to determine the amount of salt actually present in the solution in each case. The temperature of the solution has considerable effect on the solubility

[1] Read at the Pittsburg meeting of the American Chemical Society.

[2] Tower: This Journal, 22, 501 (1900).

of these salts. This effect has already been described for nickel and cobalt tartrates,[1] and is similar for the other salts used, although in most cases less pronounced. Heat seemed to decrease the solubility, so that all solutions were made up in the cold or at a temperature not exceeding 50°. The action of the dilute acids was very slow at these low temperatures. To accelerate it the solution was constantly shaken until the reaction was neutral. This required only about fifteen minutes with magnesia and the freshly precipitated hydroxides of nickel and cobalt, while for the carbonates of nickel and cobalt an hour or more was frequently necessary. Solutions of barium tartrate were prepared by neutralizing a solution of barium hydroxide with tartaric acid. Solutions containing more than 1 gram-molecule of barium tartrate in 80 liters were supersaturated. Measurements with these supersaturated solutions revealed no abnormal behavior, which is also the experience of others. Attempts were made to prepare solutions of calcium and zinc tartrates. These salts are, however, so insoluble that the solutions obtained were too weak to render the measurements of any value for the purpose of comparison.

The measurements of the electrical conductivity of the tartrates reported in my former article were made with a small combination Wheatstone-Kohlrausch bridge only 25 cm. long. All the measurements which follow were made with a meter bridge, which had been carefully calibrated. The conductivities of the tartrates of nickel and cobalt were therefore redetermined with the new apparatus. The temperature at which all the determinations were made was 18° ± 0.1°. The conductivity of the water used varied from 2.0 to 3.0×10^{-6}. This has been deducted from the specific conductivity in every case. The results with the salts of tartaric, malic and succinic acids are given in Table I: v is the number of liters in which a gram-molecule of the salt was dissolved; M is the molecular conductivity in reciprocal ohms. In the former article the equivalent conductivity was given, but since some of the salts probably exist in a polymerized condition, the molecular conductivity is given as affording a better basis of comparison.

[1] Tower: *loc. cit.*, pp. 504 and 515.

TABLE I.

Nickel tartrate.

v.	*M.*	*v.*	*M.*
10.35	9.2	13.46	12.0
2 × 10.35	13.8	2 × 13.46	16.4
4 × 10.35	20.7	4 × 13.46	22.7
8 × 10.35	30.6	8 × 13.46	29.8
16 × 10.35	44.4	16 × 13.46	45.0
32 × 10.35	62.8	32 × 13.46	61.2
64 × 10.35	81.5	64 × 13.46	81.3

Cobalt tartrate.

v.	*M.*	*v.*	*M.*
25.38	25.4	31.05	32.2
2 × 25.38	34.5	2 × 31.05	43.0
4 × 25.38	47.4	4 × 31.05	57.1
8 × 25.38	63.5	8 × 31.05	74.4
16 × 25.38	83.2	16 × 31.05	96.0
32 × 25.38	105.6	32 × 31.05	120.6
64 × 25.38	133.0	64 × 31.05	150.2

Magnesium tartrate.

v.	*M.*	*v.*	*M.*
19.95	67.4	24.37	71.9
2 × 19.95	82.0	2 × 24.37	87.7
4 × 19.95	98.1	4 × 24.37	103.0
8 × 19.95	114.6	8 × 24.37	119.2
16 × 19.95	130.5	16 × 24.37	135.1
32 × 19.95	145.8	32 × 24.37	150.0
64 × 19.95	160.7	64 × 24.37	165.9

Barium tartrate.

v.	*M.*	*v.*	*M.*
20.03	58.5	21.27	59.3
2 × 20.03	70.4	2 × 21.27	72.8
4 × 20.03	85.2	4 × 21.27	88.6
8 × 20.03	105.1	8 × 21.27	106.4
16 × 20.03	125.6	16 × 21.27	126.5
32 × 20.03	143.0	32 × 21.27	147.3
64 × 20.03	161.4	64 × 21.27	167.1

Manganese tartrate.

v.	*M.*	*v.*	*M.*
37.79	66.9	41.71	68.8
2 × 37.79	81.5	2 × 41.71	83.8
4 × 37.79	98.5	4 × 41.71	99.7
8 × 37.79	114.5	8 × 41.71	117.0
16 × 37.79	132.5	16 × 41.71	133.5
32 × 37.79	148.3	32 × 41.71	148.9

Nickel malate.[1]

v.	*M.*
14.77	14.5
2 × 14.77	17.7
4 × 14.77	22.0
8 × 14.77	28.2
16 × 14.77	37.1
32 × 14.77	51.0
64 × 14.77	69.9

Cobalt malate.

v.	*M.*
18.44	23.6
2 × 18.44	28.8
4 × 18.44	36.0
8 × 18.44	45.2
16 × 18.44	58.1
32 × 18.44	74.6
64 × 18.44	94.3

Magnesium malate.

v.	*M.*
9.74	43.3
2 × 9.74	54.7
4 × 9.74	67.4
8 × 9.74	83.0
16 × 9.74	100.1
32 × 9.74	118.3
64 × 9.74	135.0
128 + 9.74	149.0

Nickel succinate.

v.	*M.*	*v.*	*M.*
18.42	62.2	19.57	62.7
2 × 18.42	75.9	2 × 19.57	76.9
4 × 18.42	91.7	4 × 19.57	92.5
8 × 18.42	108.8	8 × 19.57	109.5
16 × 18.42	125.9	16 × 19.57	126.6
32 × 18.42	143.0	32 × 19.57	145.2
64 × 18.42	158.4	64 × 19.57	160.3

Cobalt succinate.

v.	*M.*	*v.*	*M.*
17.29	65.0	20.25	68.2
2 × 17.29	78.3	2 × 20.25	82.2
4 × 17.29	93.0	4 × 20.25	97.1
8 × 17.29	109.7	8 × 20.25	113.6
16 × 17.29	126.6	16 × 20.25	130.2
32 × 17.29	145.0	32 × 20.25	148.0
64 × 17.29	159.0	64 × 20.25	162.3

Magnesium succinate.

v.	*M.*	*v.*	*M.*
14.31	76.6	15.70	77.6
2 × 14.31	88.7	2 × 15.70	90.0
4 × 14.31	102.8	4 × 15.70	104.2
8 × 14.31	117.4	8 × 15.70	119.8
16 × 14.31	131.9	16 × 15.70	134.6
32 × 14.31	146.2	32 × 15.70	149.0
64 × 14.31	158.8	64 × 15.70	160.8

[1] Only one solution of each salt of malic acid could be prepared with the small quantity of this acid on hand.

From these results interpolations have been made graphically for $v = 16$, 32, etc., by plotting curves with the molecular conductivities as abscissas and the logarithms (base 2) of the dilutions, v, as ordinates. The interpolated values are given in Table II. In cases where the conductivity was determined in two separate solutions only the average is given in the table. The results of Walden[1] for magnesium salts of these acids are given for comparison. They have been reduced to the same units and temperature. The temperature coefficient used for this purpose was 0.027, the average value found by Arrhenius[2] for sodium salts of organic acids.

TABLE II.

Molecular conductivity of tartrates.

v.	Nickel.	Cobalt.	Magnesium.	Magnesium. (Walden.)	Barium.	Manganese.
16	12.3		63.0			
32	18.1	30.5	77.5		66.8	63.2
64	25.8	41.1	93.0	92.3	81.2	78.0
128	37.1	55.5	109.8	107.8	98.5	94.2
256	52.0	72.4	125.5	124.5	117.3	110.7
512	70.4	94.2	140.8	138.9	136.2	127.1
1024	93.0	118.0	156.0	151.5	155.0	143.9

Molecular conductivity of malates.

v.	Nickel.	Cobalt.	Magnesium.	Magnesium. (Walden.)
16	14.8	22.8	51.1	
32	18.1	27.8	63.6	
64	22.6	34.2	78.2	80.9
128	29.3	43.0	95.0	96.9
256	38.5	55.2	113.4	113.9
512	53.0	70.7	129.2	130.5
1024	72.3	90.3	146.0	145.1

Molecular conductivity of succinates.

v.	Nickel.	Cobalt.	Magnesium.	Magnesium. (Walden.)
16	59.5	63.7	78.2	
32	73.0	76.8	90.7	
64	88.0	91.2	104.8	106.8
128	105.2	107.9	120.2	121.6
256	122.3	124.6	134.7	135.6
512	139.7	142.4	148.9	147.8
1024	155.6	157.5	160.8	158.6

[1] *Zischr. phys. Chem.*, 1, 537 (1887).

[2] *Ibid.*, 4, 99 (1889).

The molecular conductivities of the tartrates of magnesium, barium and manganese do not vary from one another more than may be expected for different salts of the same acid. The conductivities of the tartrates of nickel and cobalt are, however, so small as to be of an entirely different order. The same is true of the conductivities of the malates of nickel and cobalt. The conductivity of magnesium malate is somewhat less than that of the tartrate, as was also observed by Walden. The conductivities of the succinates of nickel and cobalt present no abnormal behavior when compared with the conductivity of magnesium succinate.

Determinations of the lowering of the freezing-point were made with the apparatus described in my former article. Determinations of the freezing-point of the same solution never varied more than 0.001°, but the freezing-points of two solutions made up as nearly alike as possible gave larger differences. Since the solutions used were rather dilute, a difference of two or three thousandths of a degree would frequently make a difference of ten or twenty units in the molecular weights calculated from them. So much reliance cannot therefore be placed on the absolute or on the relative value of the results obtained by this method, as on those obtained by measuring the electrical conductivity. The depressions of the freezing-point together with the apparent molecular weights calculated from them are given in Table III.

TABLE III.

Nickel tartrate.			Cobalt tartrate.		
Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.	Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.
1.8795	0.139°	260	0.6739	0.062°	207
1.7205	0.121	273	0.6505	0.059	207
1.6450	0.117	268	0.3370	0.037	173
0.8602	0.081	202	0.3252	0.036	170
0.8225	0.076	206	0.1685	0.021	153
0.4301	0.042	193	0.1626	0.021	146
Magnesium tartrate.			Barium tartrate.		
0.8642	0.139°	118	0.7136	0.063°	216
0.8428	0.137	117	0.3568	0.036	189
0.4321	0.079	104	0.3568	0.039	174
0.4214	0.076	106	0.1784	0.020	170
0.2160	0.045	91	0.1784	0.021	162
Manganese tartrate.			Nickel malate.		
0.6130	0.083°	141	1.2912	0.147°	167

Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.
Manganese tartrate.		
0.5805	0.078°	142
0.3075	0.046	127
0.2902	0.041	135
Cobalt malate.		
1.0360	0.114°	173
0.5180	0.068	144
0.2590	0.040	123
Nickel succinate.		
0.9488	0.169°	107
0.8931	0.160	106
0.4744	0.095	95
0.4466	0.082	104
0.2233	0.049	87
Magnesium succinate.		
0.9808	0.207°	90
0.8942	0.185	81
0.4904	0.115	81
0.4471	0.098	76
0.2452	0.065	72
Nickel malate.		
0.6456	0.086°	143
0.3228	0.050	123
Magnesium malate.		
1.6060	0.244°	125
0.8030	0.130	118
0.4015	0.079	97
Cobalt succinate.		
1.0125	0.176°	110
0.8646	0.156	106
0.5062	0.094	103
0.4323	0.084	98
0.2531	0.057	85

In order to render these results more readily comparable, by means of graphical interpolation the molecular weights have been calculated for dilutions of 16 and 32 liters. These figures together with the molecular weights calculated from the simple formulas of the respective salts are given in Table IV.

TABLE IV.

	Tartrates.					Malates.			Succinates.		
	Nickel.	Cobalt.	Magnesium.	Barium.	Manganese.	Nickel.	Cobalt.	Magnesium.	Nickel.	Cobalt.	Magnesium.
Mol. wt. from formula	207	207	172	286	203	191	191	156	175	175	140
Values interpolated from Table III $v = 16$...	230	244	122	...	...	164	179	120	108	111	82
Values interpolated from Table III $v = 32$...	196	207	109	234	143	140	150	100	100	103	77

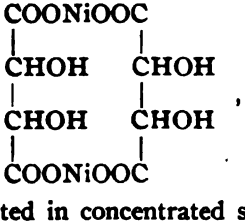
From this table it is seen that all the salts yield in the more concentrated solutions apparent molecular weights considerably less than the molecular weights calculated from the formula, except the tartrates and possibly the malates of nickel and cobalt. According to the dissociation theory we should expect all of the salts in solutions of this concentration to give apparent molecular

weights much less than the true ones. The nickel and cobalt salts just mentioned, which give such high molecular weights, are the ones calling for special explanation. These exceptional results yielded by the freezing-point method are, however, in line with the conductivity determinations with the same salts.

An adequate explanation of this peculiar behavior of the tartrates and malates of nickel and cobalt is difficult to find. It was Walden[1] who first pointed out, working with magnesium salts, that the dissociation of the salts of dibasic acids with bivalent metals as measured by the conductivity was of a very different nature from the dissociation of the neutral sodium salts of the same acids. Bredig[2] has attempted to explain this difference on the assumption that the molecules of a salt, MgAc (Ac being the radical of a dibasic acid), split up into complex ions of the nature

$$\overset{-}{\underset{+}{\overset{Mg}{Mg}}}\!\!>\!Ac \quad \text{and} \quad Mg\!<\!\overset{-}{\underset{-}{\overset{Ac}{Ac}}}$$

as well as the simpler ones $\overset{++}{Mg}$ and $\overset{--}{Ac}$. As the dilution increases the complex ions gradually tend to decompose into the simpler ones. The behavior of nickel and cobalt tartrates and malates has been shown to be very different from that of the magnesium salts of the same metals. The suggestion was made in the article to which reference has already been made, that the abnormal behavior of the tartrates of nickel and cobalt might be ascribed to polymerization of the molecules. The same would also apply to the malates. The molecule of nickel tartrate, for example, in solution would have the formula



and would be dissociated in concentrated solutions into complex ions and as dilution proceeds into simpler ones in a manner similar to that indicated above for magnesium salts, the dissociation, how-

[1] *Loc. cit.*, p. 529, *et seq.*
[2] *Ztschr. phys. Chem.*, 13, 207 (1894).

ever, being much less. This explanation differs from that of Bredig for magnesium salts in assuming the existence of *double molecules* in solution as well as of complex ions, and seems to have support in the apparent molecular weights derived from the freezing-point method.

The application of Ostwald's formula for basicity, as developed by Walden[1] for dibasic salts of bivalent metals, throws but little light on this question. The formula is $\Delta = Cn_1n_2$, where Δ is the difference between the *equivalent* conductivities at $v = 32$ and $v = 1024$, n_1 is the basicity of the acid radical, n_2 is the valence of the metal, and C is a constant, equal usually to 10 or a little less. Only molecular conductivities are given in Table II so that the difference between the values at $v = 32$ and $v = 1024$ must be divided by two to make it comparable with the difference obtained with equivalent conductivities. When this is carried out for the nickel and cobalt salts the basicity is found to be two, just the same as when applied to the magnesium salts. Since, however, the formula is wholly empirical, the results obtained by using it cannot be accepted without other support in the face of the values derived by the freezing-point method. If the Ostwald rule shows anything in this instance, it is rather to be interpreted as indicating that the complex ions decompose but little below the dilution, 1024.[2]

If then the tartrates and malates of nickel and cobalt are polymerized in aqueous solution, the molecules of the succinates are surely not, for their conductivities are normal and the apparent molecular weights found by the freezing-point method also preclude any such condition. This seems to show that the presence of the hydroxyl groups in the tartaric and malic acids may have some influence in inducing polymerization of the nickel and cobalt salts. There appears to be ground for this in the fact that the results obtained with the tartrates reveal a greater degree of polymerization than those with the malates; that is, the polymerizing influence is apparently greater where two hydroxyl groups are present than where only one is present.

[1] *Loc. cit.*

[2] From the electromotive force of a cell containing a $^1/_{50}$ molecular solution of nickel tartrate only about one-tenth of the nickel was found to exist in the ionic state. Tower: *Loc. cit.*, p. 511.

That the presence of an hydroxyl group is the determining influence in causing polymerization of the nickel and cobalt salts receives, however, no support from the results obtained by applying methods similar to the above to the malonates and tartronates of nickel and cobalt. Conductivity and freezing-point determinations were carried out with these salts and also with the magnesium salts of the same acids. The malonic acid was a preparation of Merck. The tartronic acid was made from dinitrotartaric acid according to Demole.[1] The yield was small, which accounts for only one set of determinations having been made. Molecular conductivities are given in Table V, and depressions of the freezing-point in Table VI.

TABLE V.

Nickel malonate.				Cobalt malonate.			
v.	*M.*	*v.*	*M.*	*v.*	*M.*	*v.*	*M.*
15.61	23.7	20.55	23.3	12.82	28.5	19.17	30.6
2 × 15.61	27.3	2 × 20.55	26.9	2 × 12.82	33.2	2 × 19.17	35.7
4 × 15.61	32.1	4 × 20.55	31.8	4 × 12.82	39.6	4 × 19.17	42.4
8 × 15.61	39.9	8 × 20.55	39.0	8 × 12.82	48.6	8 × 19.17	52.3
16 × 15.61	49.4	16 × 20.55	49.5	16 × 12.82	61.1	16 × 19.17	64.9
32 × 15.61	64.0	32 × 20.55	64.0	32 × 12.82	78.4	32 × 19.17	81.5
64 × 15.61	80.2			64 × 12.82	96.0		

Magnesium malonate.				Nickel tartronate.	
v.	*M.*	*v.*	*M.*	*v.*	*M.*
8.02	34.6	11.00	38.2	30.50	29.7
2 × 8.02	42.7	2 × 11.00	47.1	2 × 30.50	34.7
4 × 8.02	51.7	4 × 11.00	59.2	4 × 30.50	40.3
8 × 8.02	64.7	8 × 11.00	73.2	8 × 30.50	46.9
16 × 8.02	77.5	16 × 11.00	88.7	16 × 30.50	54.5
32 × 8.02	93.8	32 × 11.00	106.9	32 × 30.50	63.8
64 × 8.02	110.9	64 × 11.00	126.8		

Cobalt tartronate.		Magnesium tartronate.	
v.	*M.*	*v.*	*M.*
28.10	36.5	15.77	42.0
2 × 28.10	43.3	2 × 15.77	51.3
4 × 28.10	50.6	4 × 15.77	61.9
8 × 28.10	58.7	8 × 15.77	74.8
16 × 28.10	68.5	16 × 15.77	89.2
32 × 28.10	79.4	32 × 15.77	105.7
		64 × 15.77	122.5

[1] *Ber. d. chem. Ges.*, 10, 1789 (1877).

TABLE VI.

Nickel malonate.			Cobalt malonate.		
Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.	Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.
1.0300	0.150°	131	1.1995	0.201°	114
0.7824	0.141	106	0.8402	0.169	95
0.5150	0.090	109	0.5998	0.115	99
0.2575	0.054	91	0.2999	0.066	86
Magnesium malonate.			Nickel tartronate.		
1.5750	0.298	101	0.5798	0.102	108
1.1477	0.233	94	0.2899	0.065	85
0.5738	0.134	82	0.1450	0.039	71
0.2869	0.075	73			
Cobalt tartronate.			Magnesium tartronate.		
0.6302	0.119	101	0.9944	0.200	95
0.3151	0.071	85	0.4972	0.121	78
0.1576	0.043	70	0.2486	0.072	66

To bring the results of these two tables to a uniform basis, interpolations have been made graphically, exactly as in the preceding cases. These interpolated values will be found in Tables VII and VIII.

TABLE VII.

	Molecular conductivity.						
	Malonates.				Tartronates.		
v.	Nickel.	Cobalt.	Magnesium.	Magnesium. (Walden.)	Nickel.	Cobalt.	Magnesium.
16.....	23.0	30.0	43.0		25.5	32.0	42.3
32.....	26.5	34.7	52.6		29.9	37.8	51.5
64.....	31.2	41.2	65.7	62.9	35.1	44.7	62.4
128.....	38.2	51.2	79.5	77.5	40.8	52.2	75.3
256.....	47.8	64.0	95.9	95.4	47.3	60.3	89.9
512.....	61.4	80.4	113.9	114.7	59.2	70.4	106.3
1024.....	77.2	99.3	135.0	134.9	64.3	81.2	123.0

TABLE VIII.

	Malonates.			Tartronates.		
	Nickel.	Cobalt.	Magnesium.	Nickel.	Cobalt.	Magnesium.
Molecular weight from formula....	161	161	126	177	177	142
Values interpolated from Table V. $v=16$.....	121	104	87	...	...	94
Values interpolated from Table V. $v=32$.....	101	91	77	106	98	77

It is seen in these cases as heretofore, that the nickel and cobalt salts possess lower molecular conductivities and higher apparent molecular weights than the corresponding magnesium salts. Al-

though the conductivities of all these salts are less than for the corresponding succinates, still the relative differences between the conductivities of the nickel, cobalt, and magnesium salts are about the same as in the case of the succinates. No such differences exist, as were found between the conductivities of the tartrates and malates of magnesium and those of the corresponding nickel and cobalt salts. The conductivities of the magnesium salts of malonic and tartronic acids are considerably less than the conductivities of any of the other magnesium salts investigated. This was noticed by Walden in the case of the malonate. Bredig's explanation of such behavior has already been referred to. The important point to notice in connection with these last results is, however, that the conductivities of the nickel and cobalt tartronates are not appreciably less than the conductivities of the same malonates, although tartronic acid possesses an hydroxyl group. Any explanation of the conduct of these salts based on the presence of an hydroxyl group in the molecule, therefore, appears to be untenable.

Before letting the question rest here, however, a few considerations bearing upon the point under discussion will be mentioned. The strength of the acids of the succinic acid series (*i. e.*, succinic, malic, and tartaric acids), as is well known, increases with the number of hydroxyl groups present, Ostwald's affinity constants being for succinic acid 0.0066, for malic acid 0.0395, for tartaric acid 0.097.[1] The hydroxyl groups have therefore a distinct effect on the strength of the acids. In the case of malonic and tartronic acids a very different effect is observed. The Ostwald constant for malonic acid is 0.158 and for tartronic acid 0.107; that is, the introduction of an hydroxyl group has here decreased the strength of the acid. Such being the facts with regard to the acids, it seems probable that salts of the succinic acid series might show very different gradations in properties from the same salts of the malonic acid series. Then before asserting that the presence of the hydroxyl groups in malic and tartaric acids has no effect on the behavior of their nickel and cobalt salts, it is necessary to extend investigations similar to these to the salts of the glutaric acid series or some higher one. Such work is contemplated in the future.

[1] The values given are for K = 100*k*. See *Ztschr. phys. Chem.*, 3, 418 (1889).

In conclusion, however, it may be stated that aqueous solutions of nickel and cobalt salts of dibasic organic acids offer greater resistance to the passage of the electric current than solutions of similar salts of the other metals investigated, notably magnesium, and that this resistance is exceptionally great in the case of the tartrates and malates of nickel and cobalt. This abnormal behavior of the last-named salts is also confirmed by the results obtained with the freezing-point method for determining molecular weights.

WESTERN RESERVE UNIVERSITY,
CLEVELAND, O., June, 1902.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 69.]

ON THE MANGANESE FERROCYANIDES.

BY ALBERT ERNEST DICKIE.

Received August 2, 1902.

THIS work was undertaken to throw further light on the composition of the manganese ferrocyanides as seemed warranted by the discrepancies in the results obtained previously by Wyrouboff,[1] Stone and Van Ingen,[2] and Miller and Mathews.[3]

Wyrouboff, by precipitating a manganous salt with potassium ferrocyanide, obtained a compound to which he ascribes the formula $5Mn_2Fe(CN)_6.4K_4Fe(CN)_6.4H_2O$, and by using hydroferrocyanic acid he obtained the normal manganese ferrocyanide $Mn_2Fe(CN)_6.7H_2O$. In either case he found it to be immaterial which reagent was used in excess.

Stone and Van Ingen obtained results expressed in atomic ratios as follows:

	Mn.		Fe.
In neutral solution, excess ferrocyanide.....	93	:	100
" " " " manganese	95	:	100
" " " " " hot	92	:	100
" faintly acid solution, excess manganese.....	101	:	100
". more " " " "	133	:	100
" " " " " " hot.....	107	:	100

[1] *Ann. chim. phys.*, [5], 8, 474.
[2] This Journal, 19, 542.
[3] *Ibid.*, p. 547.

Miller and Mathews obtained in slightly acid solution:

With excess of ferrocyanide 105 to 108 : 100
" " " manganese 110 to 111 : 100

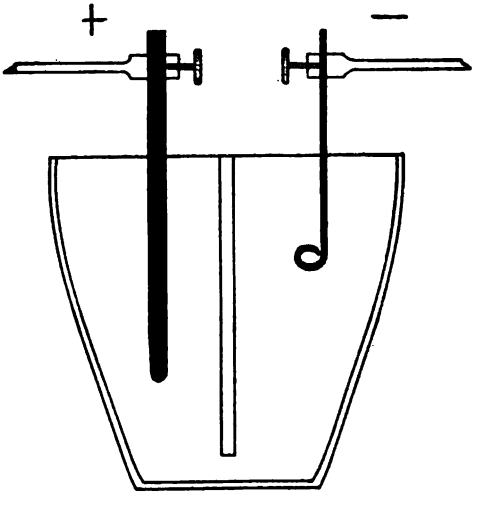
In the new series of experiments we have obtained:

	Ferrocyanide in excess. Mn.		Fe.	Manganese in excess. Mn.	Fe.
In neutral solution.....	103	:	100	107 to 108	: 100
In acid solution 10 cc. hydrochloric acid (1.20) per liter.....	106	:	100	107 to 110	: 100
In acid solution 10 cc. acetic acid (50 per cent.) per liter	101 to 102	:	100	107	: 100
In presence of ammonia and ammonium chloride	decomposed			no test for potassium	

From the above comparative statements of results the reader is left to draw his own conclusions.

NOTES.

Note on the Preparation of Metallic Lithium.—The following method is a modification of that of Bunsen and Matthiessen for



the electrolysis of fused lithium chloride, and will be found to give good results.

The apparatus consists of an ordinary porcelain crucible, about two inches in diameter and one and three-quarters inch high, fitted with a partition of asbestos-board reaching almost to the bottom.

The anode is a pencil of gas carbon which is immersed in the fused chloride on one side of the asbestos diaphragm, the cathode being of iron wire bent into the form shown and placed in the electrolyte on the other side.

A current of from 5 to 7 amperes is used from the 110-volt circuit, and in a few minutes a globule of metallic lithium will appear in the iron wire loop, which may be transferred to a vessel of kerosene by withdrawing the wire and tapping off the metal while it is still melted.

The lithium chloride must be dry and is first fused in the crucible over the gas flame, and during the electrolysis is kept in the molten condition by means of a burner placed underneath and also by the resistance of the current.

The modification was worked out mainly by one of my students, P. F. Cowing, who obtained considerable quantities of the metal in this way.

SAMUEL A. TUCKER.

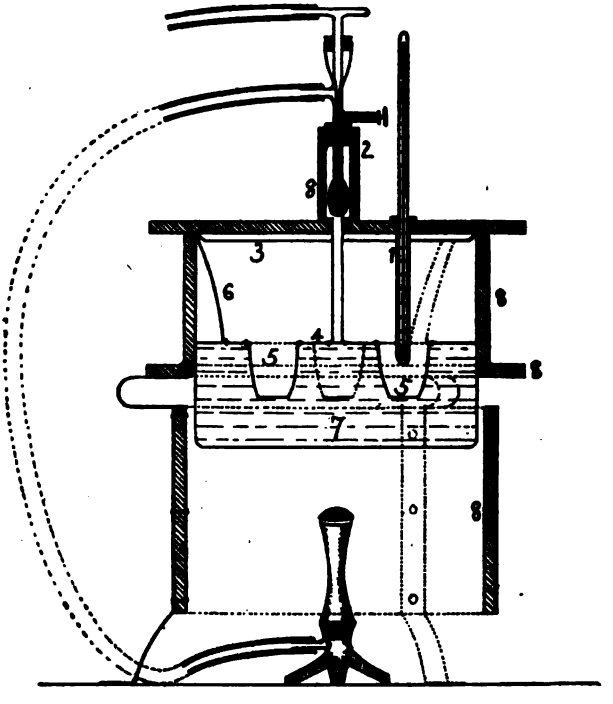
HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, May 31, 1902.

A Novel Constant High Temperature Bath.[1]—The sulphate method, exemplified by the work of G. Krüss, for the determination of the atomic weight of certain elements is open to objections, as first pointed out by Brauner and Povlicek and noted by Dennis and myself, but it answers very satisfactorily as a criterion in the fractionation of the rare earths. Our source of heat is gasoline and the gas pressure varies considerably with large classes in the laboratories. As the heating continues for days at a time, it became quite necessary to devise a bath which might be regulated and expected to remain at some fixed temperature between 350° and 450° C. The accompanying diagram shows a section of the bath designed and is really self-explanatory. It was made by Eimer and Amend and paid for in part by a grant from the American Association for the Advancement of Science to which I owe sincere thanks.

The apparatus consists essentially of a porcelain-lined water-

[1] Read at the Pittsburg meeting of the American Chemical Society.

bath with a copper flange, depressed to support the copper cover, bound to the top, and a fusible alloy. The use of a fusible alloy as a bath for moderately high temperatures is not new. The flange has three sections, 1 cm. across, cut out equidistant to permit the passage of the copper springs, which hold the iron float depressed in the molten alloy, when it is desired to remove it. The float in



Scale: 5 mm. = 2 cm.

1. Brass sheath for thermometer, graduated to 350° C.; 2. Closed iron cylinder, containing thermostat; 3. Copper cover; 4. Iron float, containing crucible molds, 5; held down by springs, 6, bearing against flange; 7. Bath of molten alloy; 8. Asbestos sheathing; 9. Asbestos cover; 10. Asbestos ring.

this particular bath has three depressions made to hold evenly platinum crucibles of 60 cc. capacity. One is for the counterpoise and the third is for the thermometer held in place by a brass sheath long enough to allow the bulb to reach the center of the depression. The three places were regarded necessary on account of danger of introducing impurities into a crucible during the inser-

tion or removal of the thermometer, which contains mercury with carbon dioxide under twenty atmospheres' pressure. The thermometer was standardized at the Reichsanstalt. The float is handled by means of a small iron cylinder rising vertically. It is much enlarged above the second cover (asbestos) to hold a short mercury thermostat made of especially resistant glass. The two covers have hit-and-miss slits that they may be taken off for removal of crucible. All exposed surfaces of the bath, except where it is heated, are jacketed with heavy asbestos. The large excess of acid sometimes used in the determinations is first driven off in a hot air platinum bath (to be described in due time) before the crucibles are placed in this bath. Notable corrosion is thus avoided. The source of heat is a complex Bunsen burner.

So far the bath has given perfect satisfaction.

CHARLES BASKERVILLE.

UNIVERSITY OF NORTH CAROLINA,
April, 1902.

On an Adulteration of Lavender Oil with Salicylic Acid.—A French lavender oil, which the following constants showed to be of good quality,

$d_{15°} = 0.893$,
$[\alpha]_D = 6° 42'$,
Acid number $= 4.48$,
Ester content $= 35.52$ per cent. as linanyl acetate,
Soluble in 2.5 vol. and more 70 per cent. alcohol,

turned red after some time, something never observed before in lavender oil. This discoloration was traced back to salicylic acid, which evidently had acted on some defective parts inside the tinned cans.

The salicylic acid was isolated from the oil by shaking the same with a potash solution of 10° Bé. Hydrochloric acid precipitated the organic acid from the alkaline solution. Another part could be obtained by extracting the filtrate with ether. The acid was purified by repeated fractional precipitation with hydrochloric acid from its alkaline solution, recrystallization out of chloroform and finally out of water with addition of some animal charcoal. The white crystals, now quite odorless, melted at 156°-157°. They were identified as salicylic acid by the characteristic violet colora-

tion with ferric chloride solution and the odor of salicyl methyl ester by heating with methyl alcohol and sulphuric acid.

The acid number of the oil indicates 1.104 per cent. salicylic acid, but as some of the acid reaction is due to the natural oil anyhow, one can guess that about 1 per cent. of salicylic acid has been added, and this is an amount, which it would hardly pay to put in. In my opinion it was a test case, to see if the sophistication would be found out, with the intention of putting more in the next time and also to use an oil of a poorer quality, anticipating that the analyst would neglect the acid number and figure the whole saponification number for esters.

The oil did not contain any salicylic ester: no fraction of the oil, distilled *in vacuo*, gave a violet color with ferric chloride solution.

An alcoholic solution of a pure lavender oil does not show any red or violet color with ferric chloride, but an oil adulterated with salicylic acid will.

The occurrence of this attempt of adulteration adds salicylic acid to the list of other materials, as succinyl methyl ester,[1] rosin[2] and benzoic acid,[3] already found in lavender oil, put in to raise the ester content found by analysis or else obscure the analysis.

J. EVERHARD WEBER.

CHEMICAL LABORATORY OF THE PROCTER AND GAMBLE CO., IVORYDALE.

The Production of Acylamines by the Interaction of Sodium Salts of Monobasic Acids and Amine Hydrochlorides.—On page 758 (August number) of this Journal, Frederick L. Dunlap publishes a paper under the above heading. Dr. Dunlap produces some aceto compounds by the action of an acetate on the hydrochlorides of various amines. He states that he is aware of the existence of United States Patents Nos. 574,395 and 574,396 "For the manufacture of acetanilide." He goes on to show that the method which he outlines is a general one. He fails to state that the patents cited make a specific point of the general nature of the reaction in question; that, in fact, the letters patent are granted, not "For the manufacture of acetanilide," but for a "Process for obtaining aceto derivatives of aromatic amines."

[1] Schimmel's Report, April, 1897, p. 24.
[2] *Ibid.*, October, 1900, p. 41.
[3] *Ibid.*, April, 1902, p. 46.

He fails to state that the inventors specifically named a number of such amines; that they did not confine themselves to the hydrochlorides, but investigated various salts of such amines, *e. g.*, the sulphates; and they also availed themselves of the well defined *acid acetates* such as $KC_2H_3O_2C_2H_4O_2$.

Dr. Dunlap entirely ignores the work of the patentees, the writer and Dr. Wm. H. Warren, on the production of such aceto compounds from mixtures of an acetate, the amine and the salt of a volatile base as indicated in the following equation:

$$RNH_2 : MC_2H_3O_2 : NH_4Cl = RNHOC_2H_3 : MCl : NH_3 : H_2O.$$

The general method of Varley[1] for the production of various amides is also set forth in Dr. Dunlap's paper without the slightest reference to the former's extended work on the subject. The method of manipulation, it is true, differs somewhat, as Dr. Dunlap works in a closed tube, while Varley worked in open vessels, on larger quantities and with better yields. Varley's work was simultaneons with that of the writer and Dr. Warren, but entirely independent.

Dr. Dunlap's statement regarding "The Literature" is true so far as our work is concerned, if one may entirely ignore the patent reports of this and foreign countries. It is not true as regards Varley's work. It would seem difficult to understand how Dr. Dunlap could have ignored Varley's work entirely and, also, the general nature of our reaction when that was fully set forth even in the title of the patent, not to speak of the broader scope of our work, embracing, as it did, salts in general, the acid salts, the use of a salt of a more volatile base and, in a general way, the influence of the amounts of the various reacting substances. The last subject was not treated at length by us for the reason that the reaction seemed to follow parallel lines with that of acetic acid and aniline as studied out by Menschutkin,—the mineral salt seeming to be more or less inert after being formed in the melt. An excess of acid and acetate over amine was beneficial, as would be expected; and a still greater excess of acetate is preferable to prevent the possibility of free mineral acid. This is, of course, provided the yield is to be calculated from the amine.

It is not necessary here to repeat the details set forth in the

[1] *Bull. Soc. Chim.*, [3], 9, 690-692; *Ber. d. chem. Ges.*, 26, R. 881.

patents referred to. It seems, however, not out of place to call attention to the reaction as worked out by Dr. Warren and the writer, since Dr. Dunlap seems to have overlooked its general nature.

R. W. CORNELISON.

BLOOMFIELD, N. J.,
August 8, 1902.

VOL. XXIV. [NOVEMBER, 1902.] No. 11.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 70.]

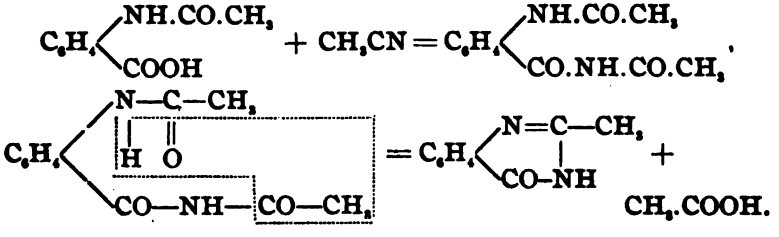
THE SYNTHESIS OF ALKYLKETODIHYDROQUINAZOLINES FROM ANTHRANILIC NITRILE.[1]

BY MARSTON TAYLOR BOGERT AND WILLIAM FLOWERS HAND.

Received July 31, 1902.

THEORETICAL PART.

BOGERT AND GOTTHELF have already shown[2] that ketodihydroquinazolines may be prepared by heating together in sealed tubes anthranilic acid, or its acyl derivatives, with a nitrile, and the reactions there suggested in explanation of this synthesis, taking the case where an acylanthranilic acid was the starting-point, were as follows:



It will be seen upon examining the structure of the hypo-

[1] Read before the New York Section of the American Chemical Society, at its meeting January 24, 1902.

[2] This Journal, 22, 129 and 522; 23, 611.

thetical intermediate product, the secondary amide, that the —CO—NH—CO— group being symmetrical should be formed equally well from RCN + R'.COOH as from R'CN + R.COOH; in other words, as the condensation takes place solely between the CN and COOH it is immaterial which radical carries the CN and which the COOH. This same secondary amide should therefore result when acetylanthranilic nitrile is heated with acetic acid, as follows:

$$C_6H_4\begin{cases}NH.CO.CH_3\\CN\end{cases} + CH_3.COOH = C_6H_4\begin{cases}NH.CO.CH_3\\CO.NH.CO.CH_3\end{cases}.$$

At higher temperatures then, acetic acid would split off, as indicated, with production of the quinazoline body, and we have in this manner prepared a number of the quinazolines in question, the products being in every case identical with the compounds obtained from anthranilic acid already described in the articles referred to.

The alkylketodihydroquinazolines may therefore be prepared either from anthranilic acid or from the corresponding nitrile. In cases where the *o*-amino acid is best obtained by saponification of the nitrile, it is convenient to be able to pass directly to the quinazoline from the nitrile without having to prepare the acid at all, thereby saving one step in the synthesis. We have thus prepared quinazolines from homoanthranilic nitrile.

The starting-point for our work was *o*-nitraniline, from which *o*-nitrobenzonitrile was prepared by the Sandmeyer reaction, the yield being excellent. The nitronitrile can be entirely freed from precipitated mineral cyanides by crystallizing from boiling carbon tetrachloride in which the latter are insoluble. This method of purification had been worked out by one of us before the article by Friedländer[1] came to our attention. The latter uses benzene as the means of separating the nitronitrile from the mineral cyanides, but we do not consider this so good a solvent as carbon tetrachloride, since the nitronitrile is much less soluble in cold carbon tetrachloride than in cold benzene, and where the latter is used much more of the compound is left in the mother-liquors. The old process of purification by distillation

[1] *Monatsh. Chem.*, 19, 627 (1898).

in a current of superheated steam may therefore be abandoned.[1]

The reduction of the nitronitrile is very readily accomplished by the use of stannous chloride and hydrochloric acid, with proper regulation of the temperature; the chloride of the aminonitrile then being precipitated by adding an excess of concentrated hydrochloric acid,[2] the tedious precipitation of the tin by hydrogen sulphide being thus wholly avoided. The free base may be recovered from its chloride by treatment with ice-cold alkali, collecting the base in ether; or, by adding an excess of strong ammonia water to the aqueous solution of the chloride the free base is immediately precipitated, and when washed well with cold water is practically pure. By this process, we have obtained yields of nearly 90 per cent. of that theoretically obtainable from the nitronitrile, and without a sign of saponification, no amide being found in any case, contrary to the experience of Pinnow and Müller,[3] Pinnow and Saemann,[4] and Friedländer.[5]

The anthranilic nitrile thus obtained was heated in sealed tubes with glacial formic acid, and with the anhydrides of acetic, propionic, normal butyric, isobutyric and isovaleric acid. With formic acid no satisfactory results were obtained. In all the other cases the quinazoline was obtained as expected, although the yields are not so good as from anthranilic acid. By using the acid anhydrides, the first products of the reaction are the acylanthranilic nitriles and the fatty acids, which then react at higher temperatures with production of the quinazolines. The presence of any water in the tubes is thus avoided and but little tar is produced.

Some of the acylanthranilic nitriles were isolated in the pure state and further investigated. Like the quinazolines obtainable from them, their melting-points *de*crease with *in*creasing molecular weight, the iso-compounds melting higher than those with normal structure. As it was possible that the formation of the quinazolines was due to a rearrangement of the isomeric acylanthranilic nitriles as follows:

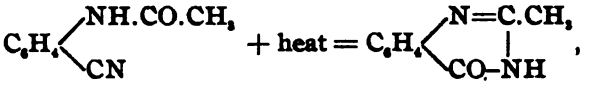
[1] Pinnow and Müller: *Ber. d. chem. Ges.*, 28, 149 (1895); Pinnow and Saemann: *Ibid.*, 29, 623 (1896).

[2] As recommended by Friedlander, *loc. cit.*

[3] *Loc. cit.*

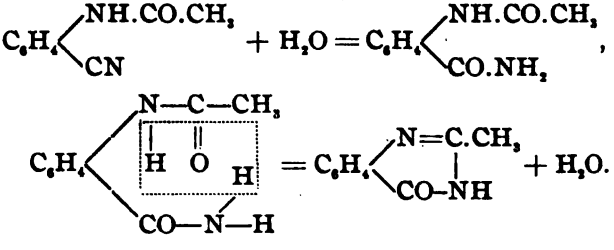
[4] *Loc. cit.*

[5] *Loc. cit.*



the acetylanthranilic nitrile, was heated for some time above its melting-point, and it was also heated in sealed tubes in toluene solution; but in neither case was any rearrangement noted. Nevertheless, some of these acylanthranilic nitriles, notably the higher ones, when in aqueous or alcoholic solution, show a decided tendency to pass over into the quinazoline, probably by addition and splitting off of the elements of water somewhat in the manner outlined in the reaction below.

Weddige[1] has already shown that acylanthranilamides can be readily condensed to quinazolines by the action of heat, acids or alkalies. As the acyl groups in these acylanthranilic nitriles are not readily split off, it seemed possible that we might pass direct from these latter substances to the quinazolines without separation of the intermediate amide and without the use of sealed tubes; and by the action of a warm alkaline hydrogen dioxide solution this change was accomplished with ease and rapidity, the yield of quinazoline usually being very large, and the only purification necessary being a single crystallization from water or dilute alcohol. Alkali alone, or hydrogen dioxide alone, we did not find to be nearly so efficient as the combination of the two. The reactions which occur in this synthesis are probably as follows:



The ease with which anthranilic nitrile may be converted into a quinazoline by the action of acetic anhydride suggests the possibility of obtaining a similar condensation by the action of acetic anhydride upon *o*-aminobenzaldoximes, the excess of anhydride changing the oxime to the nitrile when the other reactions out-

[1] *J. prakt. Chem.*, [2] **31**, 124 (1885); **36**, 141 (1887).

lined will take place with production of the quinazoline. We shall test this experimentally and communicate our results in a later article.

In conclusion, our experiments herein recorded indicate that alkylketodihydroquinazolines may be prepared:

(1) By heating anthranilic nitrile in sealed tubes with aliphatic acid anhydrides.

(2) By warming acylanthranilic nitriles with alkaline hydrogen dioxide solution.

EXPERIMENTAL PART.

o-Nitrobenzonitrile.

For the preparation of *o*-nitrobenzonitrile, the following process was found to give the best results:

13.8 grams finely pulverized *o*-nitraniline are treated with 17.5 cc. concentrated hydrochloric acid (sp. gr. 1.187) and the mass stirred until all is changed to the white chloride, taking care to crush up all lumps of *o*-nitraniline in order that the conversion to the chloride may be complete. 500 cc. of water are then added all at once and the mixture stirred thoroughly, causing the dissociation of the chloride and the separation of the free base in fine flocks which diazotize much more rapidly than the finely pulverized nitraniline. The suspended nitraniline is then diazotized by adding a solution of 7 grams sodium nitrite dissolved in 40 cc. water, stirring constantly with a turbine. No external cooling is necessary during the operation as the diazo-body is remarkably stable at ordinary temperatures, no appreciable decomposition occurring even on standing forty-eight hours at laboratory temperature, and cooling only retards the diazotizing and diminishes the yield of nitronitrile. At least one hour should be occupied in adding the sodium nitrite solution, and the mass should then be stirred for another hour, when all the orange nitraniline should be changed to the light-colored flocculent diazo-compound and starch iodide paper should still show the presence of an excess of nitrous acid. If the vessel then be allowed to stand for a few moments, any undiazotized nitraniline will collect on the bottom, and by careful decantation the suspended diazo-body may be poured off from the heavier nitraniline. Although with careful manipulation but little nitraniline escapes diazotizing, yet it is

advisable to decant from it at this point, as otherwise it follows the nitronitrile and must be separated from it later.

The suspended diazo-body is then poured very slowly into a cuprous potassium cyanide solution, prepared from 25 grams crystallized copper sulphate, 150 cc. water and 28 grams 96 per cent. potassium cyanide (carried out under a hood, on account of the cyanogen evolved). The cuprous potassium cyanide should be maintained at about 90° and stirred constantly during the addition of the diazo solution. The yield of nitronitrile depends largely upon this part of the operation. If the diazo solution is added very slowly with vigorous stirring, and the temperature kept at 90°-100°, the yield will be large; rapid addition of the diazo mixture, or allowing the temperature of the cyanide solution to sink much below 90°, diminishes the yield considerably. When all the diazo solution has been added, the mixture is boiled for a few minutes over the open flame and filtered through a hot-water funnel. On cooling, the nitronitrile crystallizes from the filtrate in long yellow needles mixed with considerable cuprous potassium cyanide. A large amount of the nitrile remains behind in what appears to be tar. By extracting this with boiling water so long as crystals separate from the filtrate, on cooling, the rest of the nitrile may be recovered. The crystals obtained by extracting the tar are practically pure and free from mineral cyanides. The actual amount of insoluble tar remaining after these extractions is very small.

The crude crystals are washed well with cold water, dried and pulverized. By extracting this dry material with boiling carbon tetrachloride, the nitronitrile is readily dissolved while the mineral cyanides remain behind absolutely insoluble. From the carbon tetrachloride filtrate, on cooling, the nitronitrile crystallizes out, almost completely, in beautiful golden yellow scales, carrying any unseparated nitraniline, and the amount of the latter substance present may be roughly judged by the depth of color of the crystals and the extent of the orange-colored ring upon the filter-paper above them when they are filtered out. By recrystallization from boiling moderately dilute acetic acid, the nitraniline is removed and the nitronitrile obtained in nearly colorless crystals (m. p. 109°). By further crystallization from dilute acetic acid, or from water, the melting-point may be raised to 109.5° at which

point it remains constant (all melting-points recorded in this article were determined with standardized short-scale Anschütz thermometers, the entire mercury column being immersed in the heating medium).

The authors have repeatedly obtained 12 grams of the crude nitronitrile from 13.8 grams of the nitraniline, a yield of 87 per cent. of the weight of the nitraniline used, and the yield is equally good when working with five to ten times the above charges. The yield of pure nitronitrile (m. p. 109.5°) amounts to about 70 per cent. of the weight of the nitraniline used. As to the amount of mineral cyanide carried down with the nitronitrile—of 285 grams crude nitrile obtained in one experiment, 28 grams consisted of mineral matter insoluble in boiling carbon tetrachloride.

The process outlined above is based upon that of Sandmeyer,[1] with certain improvements suggested by Pinnow and Müller[2] and by Friedländer,[3] together with some modifications of our own. Pinnow and Müller[4] recommend the use of much more concentrated solutions, but their process was far less satisfactory in the hands of the writers than the one given above. So little water is used in their method that the diazo solution forms a stiff paste which it is difficult to stir properly, and the yield of crude nitrile is smaller, besides being richer in mineral cyanides.

Pure *o*-nitrobenzonitrile crystallizes from dilute acetic acid or from water in feathery bunches of fine colorless needles, occasionally united in transparent films with comb-like edges; from carbon tetrachloride it crystallizes in a web of colorless dazzling tinsel-like filaments of iridescent luster, so firmly interwoven that, after pouring out the carbon tetrachloride, it may be removed from the beaker in a single mass which is not easily torn apart. It is very readily soluble in chloroform, acetone, ethyl acetate; easily in methyl alcohol, ethyl alcohol, ethyl nitrate, absolute ether, glacial acetic acid, benzene and nitrobenzene; slowly soluble in cold isoamyl alcohol, dissolving rapidly when heated; difficultly soluble in cold water, moderately soluble on boiling; very slightly soluble in cold carbon tetrachloride, quite readily in hot; difficultly soluble in cold oil of turpentine, easily in hot; difficultly soluble in

[1] *Ber. d. chem. Ges.*, 18. 1492 (1885).
[2] *Loc. cit.*
[3] *Loc. cit.*
[4] *Loc. cit.*

boiling carbon bisulphide, petroleum ether or benzine. It dissolves very slowly in cold concentrated hydrochloric acid and can be reprecipitated unchanged (m. p. 109.5°) by diluting with water.

o-Aminobenzonitrile (*Anthranilic Nitrile*).

According to our experience, the reduction of the nitronitrile can be accomplished more satisfactorily with stannous chloride and hydrochloric acid than with tin and hydrochloric acid.

The following process, based upon the method of Pinnow and Saemann[1] and embodying certain suggestions due to Friedländer[2], has given excellent results.

500 grams stannous chloride are dissolved in 425 cc. concentrated hydrochloric acid diluted with 7.5 cc. of water, and the solution is stirred vigorously with a turbine while 100 grams of the nitronitrile are gradually added at such a rate that the temperature of the solution remains at 20°-30°, occasional cooling with ice being necessary. Below 20° the reduction proceeds very slowly. As the action progresses the nitronitrile gradually dissolves, and the reduction should be complete in a few hours. If the chloride of the aminonitrile begins to separate before the completion of the reduction it can be brought into solution again by careful addition of water. When all the nitronitrile has been reduced a large volume of concentrated hydrochloric acid is added and the mixture is left for twelve to eighteen hours at 0°. Nearly all of the aminonitrile will thus be precipitated as the chloride, in fine white granular crystals which can be filtered out through asbestos. The amount of this chloride remaining in the acid mother-liquor is usually very small and not sufficient to pay for the time and trouble necessary to recover it. Of course, if the reducing solution be too greatly diluted with water, the precipitation with hydrochloric acid will be much less complete, and it may then be advisable to work over the mother-liquor. In one of our experiments there was precipitated by the hydrochloric acid an amount of aminonitrile chloride equivalent to a yield of 80 per cent. of that theoretically obtainable from the nitronitrile, while from the acid mother-

[1] *Loc. cit.*
[2] *Loc. cit.*

liquor there was recovered but 5 per cent. more, making the total yield 85 per cent. of the theoretical. The precipitated chloride is washed free from tin with concentrated hydrochloric acid, sucked as dry as possible, and the free base liberated by either of the following methods:

(1) The chloride is added to a mixture of ice and ether contained in a separatory funnel. Sodium hydroxide solution is poured in to alkaline reaction, the mixture well shaken and the ether poured off, the residual aqueous solution being extracted three or four times more with ether. The ethereal extracts are combined, dried with calcium chloride, the ether distilled off, and the brown liquid residue placed *in vacuo* over concentrated sulphuric acid where it soon solidifies in a light brown crystalline cake melting at 49° C.

(2) The chloride may be added direct to an excess of moderately dilute ammonia water, the precipitated base washed with water till free from ammonium chloride, dried and crystallized from carbon bisulphide. The yield of pure aminonitrile by this process is usually at least 85 per cent. of the theoretical. We have not observed in any case the formation of nitro- or amino-amide, the crystals which separated during reduction being invariably only the chloride of the amino-nitrile, the free base obtained from them being always instantly and completely soluble in cold benzene (in which the *o*-nitro- and *o*-aminobenzamides are difficultly soluble).

The melting-point of the crude aminonitrile is 49°; on recrystallization this may be raised to 49.5° at which point it remains constant. Friedländer[1] gives the melting-point as 50°-51°.

Pure anthranilic nitrile crystallizes in colorless glassy monoclinic prisms. By slow cooling of a carbon bisulphide solution, we have obtained some superb prisms of light yellow cast, two inches long by a quarter of an inch thick and perfectly formed. It is very easily soluble in chloroform, methyl alcohol, ethyl alcohol, ethyl nitrate, absolute ether, acetone, ethyl acetate, carbon bisulphide, benzene, nitrobenzene and pyridine; easily soluble in carbon tetrachloride and amyl alcohol; moderately soluble in cold oil of turpentine, very easily on boiling; difficultly soluble in cold water, moderately soluble at boiling-point; insoluble in cold con-

[1] *Loc. cit.*

centrated ammonia water, moderately soluble boiling; insoluble in cold petroleum ether or benzine, slightly soluble boiling. From boiling water the substance often separates as an oil which only slowly solidifies on standing. Occasionally, glassy blades may be obtained from water, but if these are left in the solution for a few days they become white and opaque and then show a lower melting-point (46°-47°). The carbon bisulphide solution is very sensitive to changes of temperature; from a solution prepared at the ordinary temperature the nitrile may be crystallized out almost completely by cooling slowly in a freezing-mixture; and large crystals which have separated by slow evaporation of the solvent at the ordinary temperature may all be redissolved quite rapidly by a slight rise in the temperature of the laboratory.

Hydrochloride of Anthranilic Nitrile.

To prepare this chloride, the nitrile was dissolved in dry ether and a stream of dry hydrochloric acid gas passed in. The chloride precipitated immediately, and was filtered out, washed with dry ether, and recrystallized from glacial acetic acid. These crystals decompose when heated slowly, but can be melted if heated quickly. They are instantly dissociated by water and give off hydrochloric acid even in the air. They dissolve quite easily in absolute alcohol, are sparingly soluble in boiling toluene, moderately soluble in glacial acetic acid (with partial dissociation), and are apparently insoluble in chloroform, carbon tetrachloride, benzene, absolute ether, ligroin or acetone.

Pinnow and Müller[1] state that this chloride crystallizes in beautiful tablets which are quite stable, although they also admit that they tend to dissociate in aqueous solution, while Pinnow and Saemann[2] attempted to separate anthranilic nitrile from the corresponding amide by crystallizing their chlorides from water. Our experience concerning the stability in aqueous solution of the chloride of anthranilic nitrile is quite at variance with these statements. In concentrated hydrochloric acid the chloride appears to be quite stable, however.

[1] *Loc. cit.*
[2] *Loc. cit.*

The Preparation of 2-Alkyl-4-ketodihydroquinazolines by Heating Anthranilic Nitrile in Sealed Tubes with Aliphatic Acids or Their Anhydrides.

(1) *Anthranilic Nitrile and Glacial Formic Acid.*—These two substances were heated together in sealed tubes for eight hours at 270°-284°, but no quinazoline could be found in the reaction product.

(2) *Anthranilic Nitrile and Acetic Anhydride.* Tube 1.—Four grams of the nitrile and 3 cc. of acetic anhydride were heated in a sealed tube for six hours at 175°, and then for five hours at 200°. There was no pressure in the tube when cold, and the contents consisted of a yellow crystalline mass of fine felted needles. This crystalline mass was repeatedly washed with ether, the residue crystallized from nitrobenzene, the crystals obtained, washed with naphtha, then with petroleum ether, dried, and recrystallized from boiling water, containing some bone-black. From the filtrate, on cooling, there separated short glassy needles of the 2-methyl-4-ketodihydroquinazoline, melting sharply at 239° and identical in all respects with that obtained by the action of acetic anhydride and acetonitrile upon anthranilic acid. A mixture of the products obtained from these two sources showed the same sharp melting-point as when the two were melted separately.

The crystals are very easily soluble in glacial acetic acid or in concentrated potassium hydroxide solution; they are difficultly soluble in petroleum ether, naphtha, carbon tetrachloride, ethyl nitrate, ether, acetic anhydride, carbon bisulphide, benzene, xylene, cymene, or concentrated hydrochloric acid; difficultly soluble in cold water, chloroform, acetone, ethyl acetate, or oil of turpentine, moderately soluble in the same solvents at the boiling-point; difficultly soluble in cold methyl, ethyl or isoamyl alcohols, glycerol, or nitrobenzene, easily soluble in the same on boiling. An alcoholic solution of the base, treated with concentrated hydrochloric acid, gives an immediate crystalline precipitate of the chloride. The latter sublimes unchanged, without melting, and is less soluble in dilute hydrochloric acid than in water. The crystals of the free base and also of the chloride frequently show a faint yellowish green cast.

Tube 2.—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for ten hours at 274°-282°, the crude product dissolved in hot alcohol, the solution bone-blacked, filtered hot, and the filtrate concentrated. On cooling, crystals of the quinazoline compound separated, melting at 237.5° to 238.5°. Some of the purified crystals (m. p. 239°) were dried to constant weight at 135° and analyzed:

I. 0.1814 gram substance gave 29.1 cc. nitrogen at 23° and 748 mm. = 17.78 per cent. nitrogen.

II. 0.2000 gram substance gave 0.4960 gram carbon dioxide and 0.0900 gram water = 67.63 per cent. carbon and 5 per cent. hydrogen.

	Calculated for $C_9H_8ON_2$.	Found. I.	II.
Nitrogen	17.50	17.78	
Carbon	67.50		67.63
Hydrogen	5.00		5.00

The *picrate,* recrystallized from water, forms yellow prisms (m. p. 207.5°-208.5°).

(3) *Anthranilic Nitrile and Propionic Anhydride.* Tube 1.—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for five hours at 250°, and then for three hours at 275°-280°. On opening the tube no pressure was evident, and the contents were dissolved in boiling alcohol, the solution bone-blacked, filtered hot, and the filtrate concentrated. On cooling, crystals separated melting at 220°-231°, brownish in color and evidently a mixture. Washed with boiling water and recrystallized from dilute alcohol, brownish crystals were obtained melting at 220°-232°. As the amount of these crystals was small, further purification was deemed useless, the reaction being evidently incomplete.

Tube 2.—This tube contained the same charge as Tube 1, but was heated for six and a half hours at 270°-280°, then two hours at 230°, and finally for six hours longer at 274°-285°. There was no pressure in the tube when cold, and the contents were repeatedly crystallized from carbon tetrachloride, yielding crystals which were easily soluble in boiling carbon tetrachloride but difficultly soluble in it cold, and which melted at 232.5°-233.5°, softening somewhat at 231°. These crystals are identical in all their properties with the 2-ethyl-4-ketodihydroquinazoline prepared from anthranilic acid, the melting-point of which is 234°.

The *picrate* melted at 193°-194°, while that obtained from anthranilic acid melted a trifle lower (191°-192°).

(4) *Anthranilic Nitrile and Normal Butyric Anhydride.* Tube 1.—The nitrile and anhydride were heated together for three hours at 160°-198°, and then for five hours at 192°-220°. The contents of the tube appeared gray and crystalline, and by extracting with boiling water, crystals were obtained melting at 198°, which, when recrystallized from water, formed fine colorless needles, identical in all their properties with the 2-*n*-propyl-4-ketodihydroquinazoline prepared from anthranilic acid.

Tube 2 contained 2.5 grams of the nitrile and 3 cc. of *n*-butyric anhydride, and was heated four hours at 130°-211°, then for seven hours at 210°-212°, and finally for three hours longer at 215°-255°. The product was dissolved in boiling alcohol, the solution bone-blacked, filtered hot, and the filtrate concentrated; on cooling, small crystals of the quinazoline separated, which, when recrystallized from dilute alcohol, melted sharply at 200°-200.8°.

The *picrate*, after repeated crystallization, showed a melting-point of 184.5°-185°. Gotthelf[1] gives the melting-point as 183°-184°.

(5) *Anthranilic Nitrile and Isobutyric Anhydride.*—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for six hours at 224°-229° and then for six and a half hours at 275°. On cooling, no pressure was evident in the tube. The crude product was worked up in exactly the same manner as described for Tube 2 above, the crystals which separated from the alcoholic solution being recrystallized from dilute alcohol. Colorless needles were thus obtained, melting at 231.5°-232°, agreeing in all their properties with the 2-isopropyl-4-ketodihydroquinazoline obtained from anthranilic acid.

The *picrate* melts at 208.5°-209.5°. The melting-point of 213°-214° recorded for this picrate by Gotthelf[2] is evidently a mistake, as we have tested his own product and found its melting-point to be 208°-208.5°.

(6) *Anthranilic Nitrile and Isovaleric Anhydride.*—2.5 grams of the nitrile and 3 cc. of the anhydride were heated for six hours

[1] This Journal, 23, 611.
[2] *Loc. cit.*

at 224°-229° and then for six and a half hours at 275°, there being no pressure in the tube when cold. The crude product was treated in the manner just described, the first crystals obtained being recrystallized from dilute alcohol, when they showed a melting-point of 194°-195°, and proved to be identical with 2-isobutyl-4-ketodihydroquinazoline prepared from anthranilic acid.

The *picrate* melted at 188.5°-189.5°. The melting-point recorded by Gotthelf[1] for the same substance is 192. It is not easy to determine the melting-points of these picrates accurately, as they generally darken and soften several degrees below the actual melting-point.

The Preparation of Acyl Derivatives of Anthranilic Nitrile.

(1) *The Action of Glacial Formic Acid upon Anthranilic Nitrile.*—Five cc. of absolute formic acid were poured over five grams of the nitrile, causing the latter to dissolve with absorption of considerable heat. The solution was gently boiled on the sand-bath for two hours and then allowed to cool. The product was a yellow crystalline cake, a portion of which when heated to 200° appeared to suffer decomposition with evolution of gas. The cake itself is composed of a mixture of various substances and we have separated from it white, warty masses easily soluble in boiling water; also long yellow needles, apparently insoluble in boiling water and difficultly soluble in boiling alcohol, together with a flocculent yellow substance soluble in 95 per cent. alcohol. None of these products could be secured in sufficient amount or purity to render an analysis of any value. The white, warty masses are evidently the formyl derivative of the nitrile, since a quinazoline can be obtained from them on treatment with warm, alkaline hydrogen dioxide solution.

(2) *The Action of Acetic Anhydride upon Anthranilic Nitrile.*—Anthranilic nitrile dissolves quite rapidly in acetic anhydride with the absorption of considerable heat; this heat is soon given off again and the solution gradually warms up to the boiling-point of the anhydride; on cooling down again a solid crystalline cake is formed. This cake is melted and gently boiled for a few hours

[1] *Loc. cit.*

on the sand-bath, the hot liquid is poured into boiling water, the mixture boiled for a few minutes and the solution filtered hot. From the filtrate, on cooling, the acetyl derivative crystallizes in long, white, silky needles (m. p. 132.5), as given by Pinnow and Saemann.[1] By heating for some time above its melting-point, no rearrangement of the compound to the isomeric quinazoline was noted. The crystals are very easily soluble in chloroform, methyl alcohol, ethyl alcohol, isoamyl alcohol, ethyl nitrate, ether, acetone, ethyl acetate, glacial acetic acid, acetic anhydride, or nitrobenzene; easily in carbon bisulphide, benzene, or oil of turpentine; moderately in carbon tetrachloride or in cold water, easily soluble in the latter at the boiling-point; insoluble in cold petroleum ether or benzine, difficultly soluble in the same at the boiling-point. Long boiling of the aqueous solution tends to prevent the crystallization of the substance, giving a milky solution which slowly deposits a fine floury sediment. It is not readily extracted from its aqueous solution by ether. From petroleum solvents, it crystallizes in pulpy masses of minute needles difficult to filter and which pack down upon the filter-paper into a sort of skin. Good crystals may be obtained from water, and also from mixtures of naphtha and chloroform, naphtha and ether, or chloroform and carbon tetrachloride. It can be slowly sublimed at 100° in colorless transparent needles, and is volatile with steam. Warmed with alkaline hydrogen dioxide solution, or heated in a sealed tube with glacial acetic acid or acetic anhydride, 2-methyl-4-ketodihydroquinazoline is produced. 2.5 grams of the acetyl derivative and 3 cc. of toluene were heated for ten hours at 274°-282° without any rearrangement of the acetyl derivative occurring. Toluene was selected as the solvent on account of its inertness and because its boiling-point is near that of acetic anhydride and acetic acid, and also because the quinazolines are difficultly soluble in it.

Once or twice, in the preparation of this acetylanthranilic nitrile, on recrystallizing the crude product from water, there was obtained a small amount of a substance crystallizing in perfect little cubes, of faint yellowish cast, which melted sharply at 91°, but the amount obtained was insufficient for further investigation.

(3) *The Action of Propionic Anhydride upon Anthranilic Nitrile.*—Five grams of the nitrile were mixed with 7 cc. of the

[1] *Loc. cit.*

anhydride. The nitrile dissolved slowly in the anhydride with absorption of considerable heat; the solution then gradually warmed up and on cooling down again solidified in a white crystalline cake. This mass was boiled gently for several hours and the product crystallized from dilute alcohol after bone-blacking. Beautiful, colorless, glassy prisms were thus obtained, melting at 119°. If heated quickly, these crystals melt much lower than this. They liquefy in boiling water. At 100°, they slowly sublime in long colorless needles. They are difficultly soluble in boiling water, nearly insoluble in cold; readily soluble in alcohol. They dissolve in cold 5 per cent. aqueous potassium hydroxide solution, and do not reprecipitate when this solution is made acid with hydrochloric acid; if an excess of strong ammonia water be then added, colorless needles of the original substance are obtained. The compound is volatile with steam. A portion was dried to constant weight *in vacuo* over concentrated sulphuric acid. This gave 16.89 and 16.44 per cent. nitrogen. Calculated for

$$C_6H_4\begin{cases}NHCOC_2H_5\\CN\end{cases}$$, 16.64 per cent.

Heated in a sealed tube with propionic anhydride, or warmed with alkaline hydrogen dioxide solution, 2-ethyl-4-ketodihydroquinazoline is produced.

(4) *The Action of n-Butyric Anhydride upon Anthranilic Nitrile.*—This reaction was carried out in a similar manner to the last, using 5 grams of the nitrile and 8 cc. of the anhydride. The nitrile dissolves slowly with absorption of heat, but does not warm up or appear to change on standing. The solution is boiled for an hour, the crude product crystallized from dilute alcohol and bone-blacked, giving colorless glassy needles or long flattened prisms. By repeated crystallization, a sharp melting-point of 89°-89.5° was recorded. These crystals are difficultly soluble in water, but easily soluble in alcohol, and volatilize with steam. With 5 per cent. aqueous potassium hydroxide solution, followed by hydrochloric acid and ammonia, this compound behaves like the propionyl derivative.

Heated in a sealed tube with *n*-butyric anhydride, or warmed with alkaline hydrogen dioxide solution, 2-*n*-propyl-4-ketodihy-

droquinazoline results. The substance is therefore the *n*-butyryl anthranilic nitrile. Long boiling in aqueous or alcoholic solution tends to change this butyryl derivative to the quinazoline.

(5) *The Action of Isobutyric Anhydride upon Anthranilic Nitrile.*—This reaction was carried out in a manner entirely similar to the last, the crude product being recrystallized from dilute alcohol till the melting-point remained constant at 111°-111.5°. The compound forms long, white, silky needles, which are slowly soluble in cold carbon tetrachloride or benzene, but easily soluble in the same on boiling; difficultly soluble in carbon bisulphide, petroleum ether, or gasoline; easily soluble in cold ether or alcohol. At 100° it slowly sublimes in colorless glistening scales. It is volatile with steam. A sample, dried to constant weight, gave the following results upon analysis: Carbon, 70.21, 70.22; hydrogen, 5.84, 5.83. Calculated for

$C_6H_4\begin{cases}NH.CQ.CH(CH_3)_2\\ CN\end{cases}$, carbon, 70.21; hydrogen, 6.38.

Heated in a sealed tube with isobutyric anhydride, or warmed with alkaline hydrogen dioxide solution, the product is 2-isopropyl-4-ketodihydroquinazoline.

(6) *The Action of Isovaleric Anhydride upon Anthranilic Nitrile.*—The reaction proceeds in the same manner as noted for the foregoing, but much greater difficulty was experienced in the purification of the crude product, repeated crystallization from dilute alcohol failing to give any substance with constant sharp melting-point. By recrystallizing from carbon tetrachloride, however, beautiful fine needles were produced, melting quite sharply at 105.5°-106.5°, and which are evidently the isovaleryl anthranilic nitrile. They are difficultly soluble in water, readily so in alcohol. In boiling water, they liquefy, and are volatile with steam. Heated in a sealed tube with *i*-valeric anhydride, or warmed with alkaline hydrogen dioxide solution, 2-isobutyl-4-ketodihydroquinazoline is the product.

A portion of the substance, dried to constant weight, gave 14.01 per cent. nitrogen. Calculated for

$C_6H_4\begin{cases}NH.CO.CH.CH_2(CH_3)_2\\ CN\end{cases}$, 13.86 per cent.

The Preparation of 2-Alkyl-4-Ketodihydroquinazolines by the Action of Warm Alkaline Hydrogen Dioxide Solution upon Acylanthranilic Nitriles.

The compounds obtained in this manner were, in every case, identical with the corresponding substances prepared from either anthranilic acid, its nitrile, or their acyl derivatives, in sealed tubes, as already described.

(1) *4-Ketodihydroquinazoline.*—Some of the crude formylanthranilic nitrile already mentioned was dissolved in 10 per cent. potassium hydroxide solution, some hydrogen dioxide solution (3 per cent.) added, and the mixture warmed at 40°-50° for an hour and a half. The solution was then filtered from a small amount of insoluble matter, the filtrate neutralized with hydrochloric acid, excess of strong ammonia water added, the solution evaporated to dryness, the residue dissolved in 99 per cent. alcohol and the solution concentrated. On cooling, crystals separated, which were filtered out, washed, dried and sublimed, giving beautiful white crystals (m. p. 215.5°-216.5°). Knape[1] gives the melting-point of 4-ketodihydroquinazoline as 211°-212°. Not sufficient of the substance was available for an analysis.

The *picrate* forms long yellow needles or plates, melting at 203.5°-204.5°, softening somewhat at 202°.

(2) *2-Methyl-4-Ketodihydroquinazoline.*—5.6 grams acetylanthranilic nitrile were mixed with 75 cc. hydrogen dioxide solution and 20 cc. of a 10 per cent. potassium hydroxide solution, and the mixture warmed at 30°-45°. In about fifteen minutes complete solution resulted, and fine white needles then began to separate, the separation being apparently complete after warming about fifteen minutes longer, since further addition of hydrogen dioxide or of potassium hydroxide caused no increase in the precipitate. These needles dissolve instantly upon the addition of a small amount of strong potassium hydroxide solution, and may be reprecipitated by carefully neutralizing with hydrochloric acid, but any excess of acid redissolves the precipitate again. From this acid solution it may be completely thrown down by adding an excess of strong ammonia water. The voluminous white pre-

[1] *J. prakt. Chem.*, (2) 43, 209 (1891).

cipitate thus obtained is crystallized from boiling water and bone-blacked, yielding beautiful glassy prisms of the 2-methyl-4-ketodihydroquinazoline (m. p. 239°). From 5.6 grams of the acetylanthranilic nitrile there was obtained 3.47 grams of the pure quinazoline compound. Some of the substance was dried to constant weight at 100°-140° and analyzed, with the following results: Carbon, 67.36, 67.32; hydrogen, 5.08, 5.02; nitrogen, 17.28, 17.47. Calculated: Carbon, 67.50; hydrogen, 5.00; nitrogen, 17.50.

When the acetylanthranilic nitrile is heated with hydrogen dioxide alone, or with alkali alone, the yield of quinazoline is not nearly so good.

The *picrate* from the above crystals separated in clusters of reddish prisms (m. p. 206°).

(3) *2-Ethyl-4-Ketodihydroquinazoline.*—1.1 grams propionylanthranilic nitrile were warmed with alkaline hydrogen dioxide solution as just indicated, the temperature being kept at 30°-65°. A clear solution was not obtained, but the propionyl derivative gradually changed to a bulky white mass of pearly scales instantly soluble in a little strong caustic alkali. The alkaline solution was treated with an excess of hydrochloric acid, then with an excess of concentrated ammonia water. The precipitate thus produced was recrystallized from water, giving fine white hairy needles of the 2-ethyl-4-ketodihydroquinazoline. The melting-point of these needles was rather low, probably because the propionylanthranilic nitrile used in the reaction was itself not perfectly pure (second-crop crystals). Recrystallization failed to raise the melting-point above 232°, while the same compound prepared from anthranilic acid melted at 234°. The yield of first-crop crystals was 0.836 gram.

The *picrate* crystallized in yellow scales (m. p. 191°-192°).

(4) *2-n-Propyl-4-Ketodihydroquinazoline.*—It was prepared from *n*-butyrylanthranilic nitrile and alkaline hydrogen dioxide solution at 30°-80°, in a similar manner to the last. The crude product was recrystallized from dilute alcohol, giving a woolly mass of fine colorless needles (m. p. 201°-202°), of 2-*n*-propyl-4-ketodihydroquinazoline.

The *picrate* crystallized in bunches of long yellow needles

(m. p. 184°-184.5°); difficultly soluble in cold water, moderately in boiling; quite soluble in cold alcohol, easily in boiling.

(5) *2-Isopropyl-4-Ketodihydroquinazoline.*—About 2 grams of the isobutyrylanthranilic nitrile, 25 cc. hydrogen dioxide solution, and 25 cc. 10 per cent. potassium hydroxide solution, were warmed together at 50°, all gradually dissolving. The solution was precipitated by hydrochloric acid, the precipitate not readily dissolving in an excess of the precipitant, and excess of strong ammonia water was then added. The bulky white precipitate which was thrown down, when recrystallized from dilute alcohol, appeared as long, colorless, silky hairs (m. p. 233°), readily identified as the 2-isopropyl-4-ketodihydroquinazoline.

The *picrate* crystallized from alcohol in yellow prisms (m. p. 208°-208.5°), at which point they turned brown and appeared to decompose. They began to darken at 205°.

(6) *2-Isobutyl-4-Ketodihydroquinazoline.*—This substance was prepared from the isovalerylanthranilic nitrile in the manner just outlined. The bulky white precipitate thrown down by ammonia water was recrystallized from dilute alcohol, giving crystals of the quinazoline, melting at 194.5°-195.5°.

The melting-point of the *picrate* was found to be 188°-189°.

In general, the yield of quinazoline obtained by the use of warm, alkaline hydrogen dioxide solution was much better than that resulting from heating the acylanthranilic nitriles in sealed tubes with anhydrides.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, June, 1902.

THE ACTION OF ISO-VALERIC ALDEHYDE UPON ANTIPYRINE.[1]

BY DAVID C. ECCLES.

Received July 14, 1902.

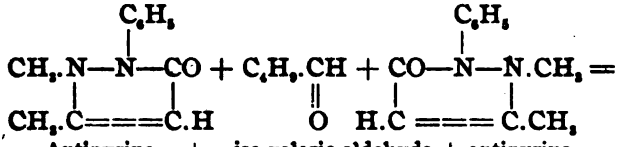
THE investigations of Knorr[2] and Schuftan[3] show that antipyrine is capable of forming condensation products with both aliphatic and aromatic aldehydes. Knorr, by treating a slightly

[1] The work here reported was done in Havemeyer Hall, Columbia University, under the direction of Prof. M. T. Bogert.

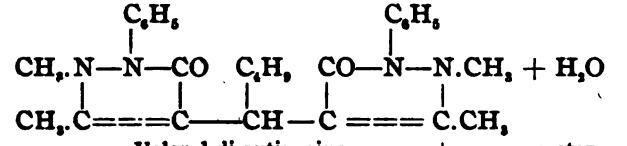
[2] *Ann. Chem.* (Liebig), 238, 214.

[3] *Ber. d. Chem. Ges.*, 1, 1181, 1189 (1895).

acid, concentrated aqueous solution of antipyrine with benzaldehyde and neutralizing, procured benzylidene-di-antipyrine. Schuftan, at a later date, by using formaldehyde instead of benzaldehyde, produced the corresponding methylene-di-antipyrine. As these condensations take place readily and give good yields of product it was concluded that 1 molecule of iso-valeric aldehyde might also combine with 2 molecules of antipyrine to give valeryl-di-antipyrine, according to this reaction:



Antipyrine + iso-valeric aldehyde + antipyrine =



Valeryl-di-antipyrine + water.

On trial this was found to be the case. The aldehyde and base, mixed in the proportion of 1 molecule of iso-valeric aldehyde and 2 molecules of antipyrine, along with enough hydrochloric acid to give a faintly acid reaction, were heated in a flask connected with a return condenser, for six hours, at 100° C., and then allowed to cool. The resulting oily liquid was poured into a small amount of concentrated potassium hydroxide solution, at once diluted with water and then stirred vigorously. After several hours' standing, an oily layer which separated changed into a white solid. This being filtered off was washed with cold water and then thoroughly dried. On crystallizing it from ligroin its melting-point was found to be 160°-161° C. The yield was about 40 per cent. of the amount calculated from the reaction cited.

The condensation here described was repeated several times and on each occasion the resulting product was composed of fine, white crystals, insoluble in cold water, slightly soluble in hot water and very soluble in alcohol. It was freely soluble in all dilutions of alcohol with water up to two of the latter to one of

the former. Hot naphtha and ligroin readily dissolved it. With hydrochloric acid this new derivative combined to form a hydrochloride and with sulphuric acid to form a sulphate. The hydrochloride was prepared by covering the condensation product with water and adding concentrated hydrochloric acid by drops. The solid slowly went into solution but, after a few minutes' standing, separated again as long, feathery needles. These were quite soluble in water and still more readily in the presence of a slight amount of hydrochloric acid. The sulphate was prepared in a similar manner from sulphuric acid but it was much less soluble and therefore separated more readily and completely.

With ferric chloride the hydrochloride gave a thick, reddish brown precipitate which dried to a brownish powder. This was soluble in alcohol and possessed a sharp astringent taste quite unlike the almost tasteless free valeryl base. This ferric derivative is analogous to ferripyrine—the ferric chloride compound of antipyrine. With Mayer's reagent both the hydrochloride and sulphate gave a white, curdy precipitate. When valeryl-di-antipyrine is warmed with concentrated sulphuric acid and sugar it gives a distinct odor like that of valerianic acid.

A determination of the nitrogen contained in valeryl-di-antipyrine gave 13 per cent. nitrogen. Calculated for $C_{27}H_{32}O_2N_4$, the nitrogen would be 12.3.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEBRASKA WESLEYAN UNIVERSITY.]

ON THE REDUCTION OF SOME AROMATIC NITRO-COMPOUNDS.

BY F. J. ALWAY AND M. D. WELSH.

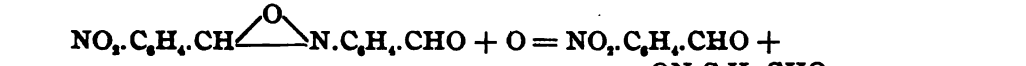
Received July 21, 1900.

IN THE following paper we give the results thus far obtained from a study of the reduction of *p*-nitrobenzaldehyde and *m*-nitrobenzaldehyde in neutral solution. As this work is for a few months necessarily interrupted and as we will be unable to continue it together we consider it best to publish the results already at hand. The investigation was undertaken in the hope that we might be able to isolate from the reduction products of the nitro-

benzaldehydes the corresponding N-formylphenyl ethers of the nitrobenzaldoximes,[1] of the formula,



As these ethers, when oxidized, give almost the theoretical yield of the corresponding nitrosobenzaldeyhdes,[2] according to the equation,



an economical method of preparing them would make the corresponding nitrosoaldehydes readily accessible compounds. The yield of these ethers obtained by the electrolytic reduction of the nitrobenzaldehydes, dissolved in concentrated sulphuric acid, is unsatisfactory, varying from 20 to 40 per cent. We failed to obtain these ethers by reduction in neutral solution. Various hydroxylaminobenzaldehyde derivatives were formed, all of which on oxidation yielded the corresponding nitroso-compounds.

In a previous article[3] one of us has described some of the phenomena observed when a solution of *p*-nitrobenzaldehyde in boiling water is treated with zinc dust.

By the action of zinc dust upon aromatic nitro-compounds in neutral aqueous or alcoholic solution, with or without addition of ammonium salts, Bamberger[4] has obtained a large number of hydroxylamino-compounds analogous to *β*-phenyl hydroxylamine, $C_6H_5NH.OH$. These are characterized by the ease with which they decompose, yielding a great variety of compounds. Wislicenus[5] has obtained the same compounds by the action of amalgamated aluminum upon the nitro-compounds in ethereal or alcoholic solution. Zinc amalgam with aluminum sulphate solution acts similarly.[6] By the oxidation of the hydroxylamine derivatives the corresponding nitroso-compounds were obtained. The latter are readily volatile with steam and, with the exception of the blue-green 3,4-dimethyl-nitrosobenzene[7] and the yellow

[1] *Ber. d. chem. Ges.*, 29, 3037 (1896).
[2] *Am. Chem. J.*, 28, 38.
[3] *Loc. cit.*
[4] *Ber. d. chem. Ges.*, 27, 1548 (1894).
[5] *Ibid.*, 29, 494 (1896).
[6] *Ibid.*, 29, 863 (1896).
[7] *Ann. Chem.* (Liebig), 316, 2857 (1901).

p-nitrosobenzaldehyde,[1] are colorless in the solid state. When fused or in solution they are green. Bamberger[2] has recently shown that 1-nitroso-2,6-xylene and nitrosomesitylene, whose cold solutions are much less intensely colored than the hot solutions, consist largely of double molecules in the former and of single molecules in the latter. Evidently the green color of the nitroso-compounds depends upon the presence of single molecules.[3] We find that *p*-nitrosobenzaldehyde, unlike the isomeric meta-compound, resembles nitrosomesitylene. Further, it is volatile with steam only when in the monomolecular condition.

The readiness with which aromatic hydroxylamines condense with aldehydes, according to the equation,

$$R.CHO + H{-}N(OH).R = R.CH(O){-}N.R + H_2O,$$

has rendered the isolation of the hydroxylaminobenzaldehydes difficult. The above reaction takes place so readily that to obtain the condensation product it is merely necessary to mix the alcoholic solutions of the compounds and allow the mixture to stand at the temperature of the room over night.

Bamberger and Friedmann[4] obtained, by the action of zinc dust upon *m*-nitrobenzaldehyde, a substance of the formula $(C_7H_5ON)_x$, which is very insoluble in all ordinary organic solvents and which, when oxidized by ferric chloride, yields, *m*-nitrosobenzaldehyde. Gattermann,[5] by the electrolytic reduction of *p*-nitrobenzaldehyde and of *m*-nitrobenzaldehyde, dissolved in concentrated sulphuric acid, obtained the two isomeric N-formylphenyl ethers of the nitrobenzaldoximes. These compounds are insoluble in ordinary solvents but may be recrystallized from pyridine. Each, on oxidation, yields together with the nitrosobenzaldehyde a small amount of what has since been found to be the corresponding azoxybenzaldehyde.[6]

Kirpal,[7] using zinc dust as a reducing agent, tried to obtain the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime. In this he was

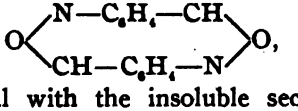
[1] *Ber. d. chem. Ges.*, 29, 3037 (1896).
[2] *Ibid.*, 34, 3877 (1901).
[3] *Ztschr. phys. Chem.*, 26, 50.
[4] *Ber. d. chem. Ges.*, 28, 250 (1895).
[5] *Ibid.*, 29, 3037 (1896).
[6] *Am. Chem. J.*, 28, 34.
[7] *Ber. d. chem. Ges.*, 30, 1597 (1897).

not successful but obtained a yellow solution which on oxidation yielded *p*-nitrosobenzaldehyde.

Later, Kalle & Co.[1] patented a process for the preparation of aromatic hydroxylamine compounds by the treatment of nitro-compounds with zinc dust and an aqueous solution of an ammonium salt in the cold. It was stated that *p*-hydroxylaminobenzaldehyde, like various other hydroxylamine derivatives, was obtained by this method in quantitative yield. No details of the method and no description of the aldehyde were given. By this method phenylhydroxylamine may be obtained in almost quantitative yield but we were unable to obtain a satisfactory yield of the hydroxylaminobenzaldehyde.

Our knowledge of the hydroxylamino- and nitrosobenzaldehydes, may, accordingly, be summarized as follows: *m*-nitrobenzaldehyde and *p*-nitrobenzaldehyde, when subjected to electrolytic reduction in concentrated sulphuric acid solution, yield the corresponding N-formylphenyl ethers of the nitrobenzaldoximes, which, by oxidation with ferric chloride, give *m*-nitrosobenzaldehyde and *p*-nitrosobenzaldehyde. The same aldehydes when reduced by zinc dust form substances of unknown nature, which, by oxidation, yield nitrosobenzaldehydes identical with those mentioned above.

While we obtained various condensation products of the hydroxylaminobenzaldehydes neither of the above-mentioned insoluble ethers was detected among the reduction products. The insoluble compound obtained by Bamberger and Friedmann,[2] from *m*-nitrobenzaldehyde evidently has the formula,



and is not identical with the insoluble secondary product of electrolytic reduction as has been suggested.[3] *p*-Nitrobenzaldehyde forms a similar compound together with one or more insoluble condensation products of *p*-hydroxylaminobenzaldehyde.

EXPERIMENTAL.

Kirpal[4] boiled 200 cc. of water with 4 grams *p*-nitrobenzalde-

[1] D. R. P. 899,781: *Chem. Centrbl.*, 1, 351 (1897).
[2] *Loc. cit.*
[3] *Ber. d. chem. Ges.*, 29, 3037 (1896).
[4] *Loc. cit.*

hyde and 20 grams zinc dust for three minutes. A yellow solution was obtained, from which, by oxidation with ferric chloride solution, *p*-nitrosobenzaldehyde was obtained and from which, by the action of the air, *p*-azoxybenzaldehyde was formed. He was unable to isolate the hydroxylaminobenzaldehyde. Our repetition of Kirpal's work confirmed his results. The residue of zinc dust was colored slightly yellow. Attempts to extract this yellow substance with boiling water yielded *p*-azoxybenzaldehyde and a compound crystallizing in red needles and melting at 222° which has not been further investigated. By using benzene, instead of water, only *p*-azoxybenzaldehyde was obtained.

That these are decomposition products of the substance that colors the zinc dust yellow is evident from the fact that when covered with a great excess of ferric chloride solution and subjected to distillation with steam, *p*-nitrosobenzaldehyde was obtained. Neither of the two substances mentioned, when treated in the same manner, gave a nitroso-compound. That the nitroso-compound, in this case, does not result from the oxidation of the simple hydroxylaminobenzaldehyde may be seen from the following. The residue was treated with boiling alcohol and filtered. The filtrate was yellow in color. With ferric chloride it gave a very small quantity of *p*-nitrosobenzaldehyde, and when shaken with sodium hydroxide solution in contact with the air, *p*-azoxybenzaldehyde was formed. Using the same amount of alcohol in each case the extraction was repeated four times. Each of the solutions (except the last), so obtained, had the same color and gave the same oxidation products. The last was almost colorless and the zinc dust showed no trace of yellow. No *p*-nitrobenzaldehyde could be obtained from the oxidation products by recrystallizing them from glacial acetic acid.

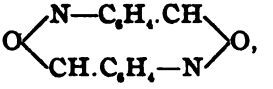
By using ammonium chloride the reduction product was obtained free from unchanged zinc. The latter, when present, seriously interferes with the investigation of the insoluble reduction product. A mixture of 10 grams *p*-nitrobenzaldehyde, 10 cc. alcohol, 30 cc. water and 10 cc. 2N ammonium chloride solution was warmed to 70°. Ten grams of zinc dust were added and the mixture violently agitated three to four minutes, keeping the temperature at 70°. The mixture became green, then yellow.

The whole was at once filtered under suction. The filtrate was light red in color and the residue yellow. The latter was extracted with 100 cc. boiling alcohol. The filtrate from this resembled the first except that the color was of a lighter shade. By the addition of water to these two filtrates we obtained a yellow crystalline substance, soluble in alcohol, ether, benzene and hot water. Aqueous alkalies imparted a deep red coloration to its aqueous and alcoholic solutions, from which the color slowly faded, *p*-azoxybenzaldehyde separating out. With ferric chloride solution it gave *p*-nitrosobenzaldehyde. It was unstable when exposed to the air in moist condition, various red and yellow compounds being formed. On account of the ease with which it underwent decomposition we failed to obtain it in pure condition from the limited amount of *p*-nitrobenzaldehyde that we had at our disposal. A nitrogen determination was made of a specimen obtained by recrystallizing the crude substance from absolute alcohol and drying the crystals at once. It melted at 98° to 101°. Calculated for $HO.NH.C_6H_4.CHO$, N = 10.2. Found, 10.1. It was evidently *p*-hydroxylaminobenzaldehyde,

$$C_6H_4\begin{cases}NH.OH\\CHO\end{cases}$$

The yellow residue of zinc oxide remaining after the treatment with alcohol was extracted six times with boiling alcohol, using 100 cc. each time. All the filtrates so obtained, acted alike. All were yellow in color, gave no precipitate with water, gave *p*-nitrosobenzaldehyde with ferric chloride and *p*-azoxybenzaldehyde with aqueous alkalies. No *p*-nitrobenzaldehyde was obtained by the oxidation. The residue was still yellow in color. It was extracted twice with boiling benzene and the cooled filtrates treated with ligroin. The first gave a yellow precipitate, the second was colored yellow but gave no precipitate and on complete evaporation left only a trace of yellow solid. The residue of zinc dust was colored brown. It was extracted twice with boiling alcohol without any sign of the extraction being complete. Both of these filtrates were similar to the other alcoholic filtrates in color and reactions. The yellow compound precipitated from benzene by ligroin melted at 205° to 206° and was very sparingly

soluble in boiling alcohol, forming a yellow solution which gave the characteristic red coloration with aqueous alkalies, and yielded *p*-nitrosobenzaldehyde but no *p*-nitrobenzaldehyde when oxidized by ferric chloride. This compound, which was also obtained in small quantity by the action of amalgamated aluminum upon *p*-nitrobenzaldehyde in ethereal solution, has not been further investigated. The brown residue on oxidation yielded *p*-nitrosobenzaldehyde. It gave no *p*-nitrobenzaldehyde when covered with dilute sulphuric acid and treated with steam. The substance causing the brown color did not dissolve in boiling pyridine. It is evident from the above that there was, at most, no appreciable amount of the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime among the reduction products. The yellow and brown substances were condensation products of *p*-hydroxylaminobenzaldehyde, the former being probably



which, when warmed with aqueous alcohol, changes partly into the simple hydroxylaminobenzaldehyde, according to the equation

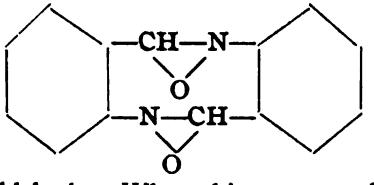
$$C_{14}H_{10}O_2N_2 + 2H_2O = 2C_7H_7O_2N.$$

If the mixture of *p*-nitrobenzaldehyde, alcohol, water and ammonium chloride solution be kept at 16° to 18° and the zinc dust added in small portions in the course of two hours, frequently shaking the mixture, the same compounds are obtained but the amount of the condensation products is less. If the mixture of all the compounds be made in the cold and left to itself the temperature rises until the liquid boils violently. The reaction product is brown in color and reacts in the same manner as the insoluble condensation product already described.

By the action of amalgamated aluminum upon the ethereal solution of *p*-nitrobenzaldehyde, similar condensation products were obtained.

m-Nitrobenzaldehyde, when treated in the same manner, yielded a brownish yellow solution from which *m*-nitrosobenzaldehyde and *m*-azoxybenzaldehyde were obtained by methods analogous to those used in the case of the para-compounds. Mixed with the zinc oxide and unchanged zinc was the gray substance, insoluble

in solvents, which Bamberger and Friedmann have found to have the formula $(C_7H_5ON)_x$. Analogous to the para-compound it gave a yellow solution when boiled with aqueous alcohol. The alcoholic solutions, so obtained, yielded small amounts of *m*-nitrosobenzaldehyde and *m*-azoxybenzaldehyde. The insoluble substance is probably the inner anhydride of *m*-hydroxylaminobenzaldehyde,



p-Nitrosobenzaldehyde.—When this compound is prepared by the oxidation of the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime the yield varies from 10 to 15 per cent. of the weight of *p*-nitrobenzaldehyde reduced. It is much more readily obtained as follows: The red colored solution, described above, containing *p*-hydroxylaminobenzaldehyde is at once treated with an excess of 10 per cent. ferric chloride solution and allowed to stand for a few hours. The yellow *p*-nitrosobenzaldehyde gradually separates out. Steam is passed through the mixture, the nitroso compound being carried over. The yield varies from 15 to 20 per cent. of the weight of the nitrobenzaldehyde used. The yield may be increased by oxidizing the insoluble condensation products.

The liquid that collects in the receiver, when this compound is separated from the ferric chloride by distillation with steam, is deep green in color. On cooling, the color gradually disappears, the yellow nitroso-compound separating out. If this is filtered out and dried at a low temperature it sometimes shows a distinctly green tint. The filtrate, if the mixture has been allowed to stand long enough, is colorless. By recrystallizing the nitrosobenzaldehyde, from glacial acetic acid, yellow needles are obtained. When these are dried and boiled with water they do not dissolve, the liquid remaining colorless. If a current of steam be passed through the boiling mixture of water and *p*-nitrosobenzaldehyde, the same result is not always observed. Sometimes no nitroso-compound is carried over with the steam, while at other times it passes over very slowly, collecting in the receiver as a green solu-

tion from which, on cooling, very little nitrosobenzaldehyde separates. In one experiment in which the distillate was colorless after steam had been passed through the mixture for some time, finely divided calcium chloride was added in small portions, a burner being kept under the distilling flask. When the temperature in the latter had thus been raised to 130° the *p*-nitrosobenzaldehyde floated unchanged on the surface of the liquid. The addition of the next portion of calcium chloride, which raised the temperature to 140°, caused the nitroso-compound to pass over very rapidly. Very impure specimens of the nitrosoaldehyde were purified by adding them to this calcium chloride solution which was kept at the boiling-point while steam was passed through. When the mixture of water and *p*-nitrosobenzaldehyde collecting in the receiver in the preparation of the latter is divided into two portions and the one immediately subjected to the action of a current of steam while the other is allowed to stand ten or twelve hours before undergoing similar treatment, a marked difference is to be noticed. In the case of the first the nitrosobenzaldehyde passes over rapidly but in the second very slowly. It dissolves in hot solvents, as acetic acid, alcohol and acetone with a deep green color. As these cool, the color slowly changes to yellow with or without separation of crystals. While the green color usually disappears within a few hours it sometimes remains for several days. As *p*-nitrosobenzaldehyde melts at 137° it would necessarily pass into the green or monomolecular condition when brought into contact with the calcium chloride solution boiling at 140°.

m-Nitrosobenzaldehyde, unlike the isomeric para-compound, is colorless in the solid state, distils readily with steam and dissolves in cold solvents with a deep green color.

UNIVERSITY PLACE, NEB.,
June 20, 1902.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEBRASKA WESLEYAN UNIVERSITY.]

ON THE NITRATION OF BENZYL CHLORIDE.

BY FREDERICK J. ALWAY.

Received July 21, 1902.

WHILE the three nitrobenzyl chlorides are well-known compounds and the action of fuming nitric acid upon benzyl chloride

has been described by different investigators, no definite information has been furnished as to the yield of *p*-nitrobenzyl chloride obtained at different temperatures. There is, also, little agreement as to the nature of the oily by-product.

Beilstein and Geitner[1] were the first to obtain *p*-nitrobenzyl chloride from benzyl chloride. Grimaux[2] repeated their work. Strakosch[3] improved the method by keeping the temperature at —15° during the operation. The later investigators, Abelli,[4] Nölting[5] and Klumpf,[6] followed the method of Strakosch. As attempts made in this laboratory to verify the statement of Strakosch, that very little except *p*-nitrobenzyl chloride is obtained at the above-mentioned temperature and that the oily by-product consists essentially of unchanged benzyl chloride, were unsuccessful, various nitration methods were tried in order to determine the conditions under which the maximum yield of *p*-nitrobenzyl chloride is obtained. It was found that the yield of *p*-nitrobenzyl chloride under the most favorable conditions, was 50 per cent. of the theoretical and that the oily by-product obtained by the different methods consists of nitrobenzyl chlorides, in some cases mixed with dinitrobenzyl chloride. If a mixture of slightly more than the theoretical amount of fuming nitric acid with concentrated sulphuric acid be added to cooled benzyl chloride a very low temperature is not required to ensure the maximum yield. If a considerable excess of fuming nitric acid be used, dinitrobenzyl chloride is formed. Ordinary concentrated nitric acid may be used instead of the fuming acid, the yield of *p*-nitrobenzyl chloride, however, being less.

EXPERIMENTAL.

The crude nitration product obtained in each of the cases described below, was added to a mixture of ice and water. The more or less pasty solid, so obtained, was transferred to a Büchner funnel and subjected to powerful filtration until oily drops ceased to pass through. The residue, when recrystallized

[1] *Ann. Chem.* (Liebig), 139, 337 (1866).
[2] *Ibid.*, 143, 46 (1868).
[3] *Ber. d. chem. Ges.*, 6, 1059 (1873).
[4] *Ibid.*, 16, 1232; *Gazz. chim. ital.*, 13, 97 (1883).
[5] *Ber. d. chem. Ges.*, 17, 385 (1884).
[6] *Ann. Chem.* (Liebig), 224, 96 (1884).

from alcohol, gave pure *p*-nitrobenzyl chloride. By treating the mother-liquor with water a further yield was obtained. In estimating the yield of solid and liquid nitration products, the residue, without further treatment, was weighed, while the liquid was washed with water, separated and dried before weighing.

Three hundred grams of fuming nitric acid (sp. gr. 1.5) were placed in a flask surrounded by a mixture of ice and salt. Benzyl chloride was added drop by drop. As each drop came in contact with the acid a reddish brown coloration was produced. At first this coloration quickly disappeared but as the addition of benzyl chloride proceeded the color disappeared more and more slowly until, after 120 grams of benzyl chloride had been added, it remained. During the operation the temperature was kept at —15° to —13°. Yield of solid, 85 grams; of liquid, 85 grams. Time required, two hours and thirty minutes. The yield of the two products was the same when the temperature was kept at —25°, as well as when fuming nitric acid was added to benzyl chloride kept at —15°. At 20° to 30° the yield of the solid was only half so great and of liquid half as great again.

The following was found to be the most satisfactory method of obtaining *p*-nitrobenzyl chloride. A mixture of 90 grams fuming nitric acid and 180 grams concentrated sulphuric acid was added to 120 grams benzyl chloride, kept at —5° to —10°. After about half the acid mixture had been added, white crystals began to separate. At the end of the operation the contents of the flask were almost solid. Yield of solid, 85 grams; of liquid, 87 grams. Time required one hour and ten minutes At temperatures above 0° the yield was less.

To determine the action of a considerable excess of fuming nitric acid, 40 grams of benzyl chloride were added to a mixture of fuming nitric acid (80 grams) and concentrated sulphuric acid (180 grams). The temperature was kept below 40°. After being allowed to stand two hours the mixture was poured into ice water. An oily liquid separated. This passed through the filter, leaving no residue. It was washed well with water, dried with calcium chloride, filtered and analyzed. It consisted essentially of one or more dinitrobenzyl chlorides.

The specific gravity and the nitrogen content were determined

in the case of each of the oily liquids obtained by the above methods.

	Calculated for $NO_2.C_6H_4.CH_2Cl$.	Calculated for $(NO_2)_2C_6H_3.CH_2Cl$.	Found. I.	II.	III.
Nitrogen	8.2	12.9	8.7	8.6	12.1
Specific gravity at 27°	..	..	1.333	1.332	1.476

From the above it is evident that not only is the yield of *p*-nitrobenzyl chloride practically the same but that the by-products are also the same, whichever of the two methods of preparing *p*-nitrobenzyl chloride is employed. The further investigation of the dinitrobenzyl chloride was not proceeded with as Cohn and Friedlander[1] have recently obtained *o*-*p*-dinitrobenzyl chloride by an analogous method and have announced their intention of soon publishing the details of their work.

UNIVERSITY PLACE, NEB.,
June 16, 1902.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA].

CONDENSATION OF CHLORAL WITH THE NITRANILINES.

BY ALVIN S. WHEELER AND H. R. WELLER.

Received July 28, 1902.

CHLORAL forms condensation products readily with aromatic amines according to the equation

$$CCl_3CHO + 2RNH_2 = CCl_3CH(NHR)_2 + H_2O.$$

O. Wallach[2] effected the condensation of chloral with aniline, the product being trichlorethylidenediphenylamine,

$$CCl_3CH(NHC_6H_5)_2.$$

In 1898 Eibner[3] and Baskerville, working independently, carried out the condensation of chloral with *p*-nitraniline. Baskerville's results are incorporated in the present paper. Our investigation shows that similar products are obtained with ortho- and meta-nitraniline. The melting-points of the condensation products form an ascending series as in the nitranilines. The chloral used was prepared by distilling chloral hydrate with concentrated sulphuric acid and the nitranilines were recrystallized until pure.

Trichlorethylidenedi-o-nitrophenamine,

[1] *Ber. d. chem. Ges.*, 35, 1266 (1902).
[2] *Ann. Chem.* (Liebig), 173, 278.
[3] *Ibid.*, 302, 366.

$CCl_3CH(NHNO_2C_6H_4)_2$. —Five grams of *o*-nitraniline were suspended in 75 cc. of benzene and 5 grams of chloral were added. Two and one-half grams of chloral are required by theory. The crystalline nitraniline was quickly converted into a flocculent precipitate which melted at 162°. The benzene solution was evaporated down to a gummy mass on the water-bath, the residue was taken up with boiling alcohol and, upon cooling, a beautiful yellow crystalline precipitate settled out. The two precipitates were recrystallized from hot alcohol until the melting-point was raised to 171°. A determination of chlorine gave 26.10 per cent. Calculated for $C_{14}H_{11}O_4N_4Cl_3$, 26.22 per cent.

Trichlorethylidenedi-*o*-nitrophenamine crystallizes from hot alcohol in yellow transparent rectangular plates and melts at 171°. It is insoluble in ether and ligroin but soluble in acetone, chloroform and benzene. It may be purified by dissolving in glacial acetic acid and precipitating with water. It is not decomposed by water and is insoluble in hot hydrochloric acid. The yield was about 45 per cent. of the theory.

Trichlorethylidenedi-m-nitrophenamine, $CCl_3CH(NHNO_2C_6H_4)_2$.—Five grams of *m*-nitraniline were suspended in 125 cc. benzene and 5 grams of chloral were added. The needle crystals of *m*-nitraniline were quickly converted into a flocculent precipitate, at first yellowish white but soon assuming a rich flesh color which was permanent. The crude substance decomposed at 208°. On digestion with acetone the impurities were dissolved out and the melting-point was raised to 212°. A determination of chlorine gave 26.18 per cent. Theory requires 26.22 per cent.

Trichlorethylidenedi-*m*-nitrophenamine crystallizes from alcohol in rectangular plates of a rich flesh color. It melts at 212°. It is readily soluble in alcohol and insoluble in ether, ligroin and benzene. It is decomposed by hot water and by hydrochloric acid, chloral and *m*-nitraniline being re-formed. The yield of the condensation product is about 30 per cent of the theory.

The reaction seems to run a different course if the materials are boiled for some time under a reflux condenser. Under these circumstances a body is obtained which, upon recrystalling once from alcohol, melts at 89°. A single analysis for chlorine showed

the presence of 32.3 per cent. This substance will be examined further.

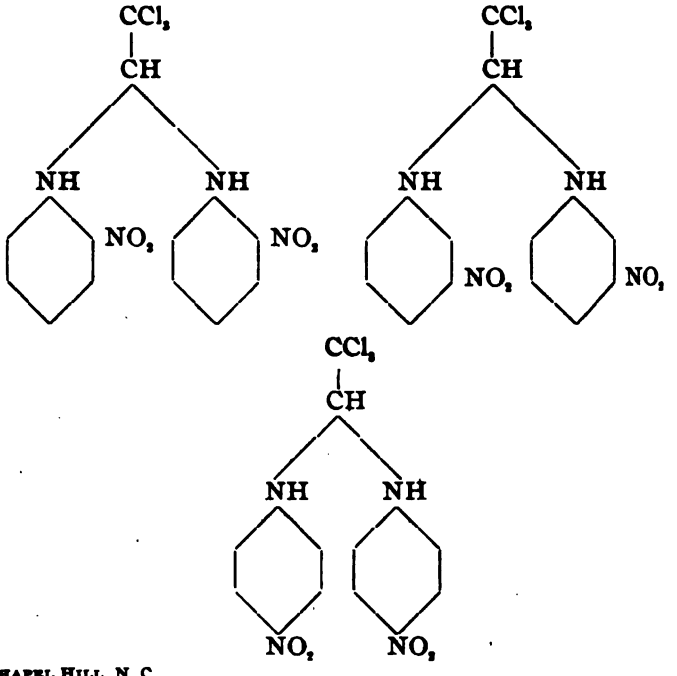
Trichlorethylidenedi-p-nitrophenamine, $CCl_3CH(NHNO_2C_6H_4)_2$.—Ten grams of *p*-nitraniline were suspended in 100 cc. benzene, and 15 grams of chloral were added slowly. A heavy yellow precipitate formed immediately. After heating for some time on the water-bath to complete the reaction, the precipitate was filtered off and dried. The melting-point of the crude substance was 210°. It is extremely insoluble and by removing the impurities with small amounts of cold acetone the melting-point was raised to 216°. A determination of the chlorine gave 26.35 per cent. Calculated, 26.22 per cent.

Trichlorethylidenedi-*p*-nitrophenamine is a yellow powder of very great insolubility. It is insoluble in water, alcohol, ether, ligroin and benzene. It is somewhat soluble in acetone and readily soluble in boiling nitrobenzene. The yield was 14.51 grams or nearly 54 per cent. of the theory. It is slowly decomposed by hot hydrochloric acid. Its conversion by acetic anhydride into *p*-nitroacetanilide and by benzoyl chloride into benzoyl *p*-nitroanilide, asdescribed by Eibner, was carried out.

Reduction of the Nitroamines.—We have tried to reduce these nitroamines with various reducing agents but so far without success. If the nitro-group could be reduced, the resulting amine might again react with chloral, forming a complex ring body. Interesting results were obtained when the nitroamines were boiled with ammonium sulphide in alcoholic solution. In each case a volatile substance condensed on the walls of the reflux air condenser in white crystals. In the case of the para-compound, these crystals melted at 120° and were insoluble in water and alcohol, but dissolved readily in carbon disulphide. This group of bodies will be studied further in this laboratory.

In naming these compounds Eibner places the "di" after the "nitro" but it seems preferable to us to place it before the "*p*".

Constitution.—In the reaction between chloral and the nitranilines it might be possible for the oxygen to combine with hydrogen in the ring, leaving the amino groups untouched. But these substances do not possess any basic properties; hence they are to be represented as follows:



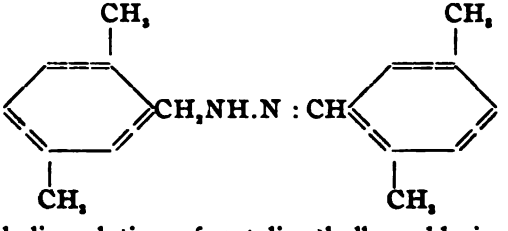
CHAPEL HILL, N. C.,
July 24, 1902.

PREPARATION OF 2,5-DIMETHYLBENZYL-2,5-DIMETHYLBENZAL HYDRAZONE AND ITS BENZOYL AND ACETYL DERIVATIVES.

BY EVERHART PERCY HARDING AND EDGAR W. RICE.

Received August 11, 1902.

2,5-Dimethylbenzyl-2,5-dimethylbenzal Hydrazone,



To an alcoholic solution of 2,5-dimethylbenzaldazine, prepared according to Curtius and Jay,[1] was added more than the calculated

[1] *J. prakt. Chem.*, 89, 43.

amount of a 4 per cent. sodium amalgam sufficient to reduce the aldazine to its corresponding hydrazone. This was heated in a flask connected with a reflux condenser for from three to four hours upon a water-bath. The solution, nearly colorless, was then filtered and the filtrate left in a freezing-mixture of salt, ice and water until the hydrazone crystallized out. The hydrazone was then filtered off, washed with water and recrystallized from alcohol. It melted at 74°-78° (uncorr). The reaction takes place according to the following equation:

$$(CH_3)_2C_6H_3CH : N.N : CH.C_6H_3(CH_3)_2 + H_2 = (CH_3)_2C_6H_3CH_2.NH.N : CH.C_6H_3(CH_3)_2.$$

The analysis gave: C, 81.03; H, 8.21. Calculated: C, 81.2; H, 8.04.

2,5-Dimethylbenzyl-2,5-dimethylbenzal hydrazone is soluble in ether, chloroform, benzene, carbon bisulphide, toluene, ethyl alcohol, methyl and amyl alcohols. It is insoluble in water. The hydrazone is very unstable and begins to decompose at once when exposed to the air.

Acetyl 2,5-dimethylbenzyl-2,5-dimethylbenzal Hydrazone,

$$(CH_3)_2C_6H_3CH_2N(C_2H_2O)N : CHC_6H_3(CH_3)_2.$$

To a concentrated alcoholic solution of the hydrazone was added a slight excess of acetic anhydride and the solution evaporated slowly to dryness upon a water-bath. The residue was recrystallized from alcohol. It gave long, white, satin-like needles which melted at 137°.

The analysis gave 9.11 per cent. N. Calculated, 9.09 per cent.

The acetyl derivative is soluble in benzene, toluene, ether, chloroform, carbon disulphide, acetic acid and in hot ethyl, methyl, and amyl alcohols. It is insoluble in water.

Benzoyl 2,5-dimethylbenzyl-2,5-dimethylbenzal Hydrazone,

$$(CH_3)_2C_6H_3CH_2N(C_6H_5CO)N : CHC_6H_3(CH_3)_2.$$

A slight excess of benzoyl chloride was added to a concentrated alcoholic solution of the hydrazone and the solution evaporated to dryness upon a water-bath. The residue was recrystallized from alcohol. Long satin-like crystals formed which melted at 134°-134.5°.

The analysis gave 7.60 per cent. N. Calculated, 7.57 per cent.

The benzoyl derivative is soluble in benzene, toluene, ether,

chloroform, carbon disulphide, acetic acid and in hot ethyl, methyl, and amyl alcohols. It is insoluble in water.

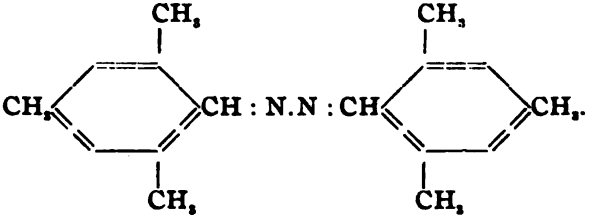
Nitroso and picric acid derivatives are at present being prepared.

PREPARATION OF 2,4,6-TRIMETHYLBENZALDAZINE; OF 2,4,6-TRIMETHYLBENZYL-2,4,6-TRIMETHYLBENZAL HYDRAZONE AND SOME OF ITS DERIVATIVES.

BY EVERHART PERCY HARDING.

Received August 11, 1908.

2,4,6-Trimethylbenzaldazine,



2,4,6-Trimethylbenzaldazine was prepared by adding to a weak alcoholic solution of 2,4,6-trimethylbenzaldehyde, which was prepared according to Gattermann,[1] a solution of hydrazine sulphate containing the calculated amount of sulphate to produce the corresponding aldazine. The mixed solutions were warmed to 60°, violently shaken for thirty minutes and allowed to stand for two hours. The yellow substance that separated formed spherulitic masses which recrystallized from acetic acid in beautiful light yellow prisms which melted at 167°.

$$(CH_3)_3C_6H_2CHO + H_2N'NH_2 + OHCC_6H_2(CH_3)_3 = (CH_3)_3C_6H_2.CH : N.N : CH.C_6H_2(CH_3)_3.$$

These gave 9.59 per cent. N. Calculated, 9.56 per cent.

2,4,6-Trimethylbenzaldazine is very soluble in chloroform. It is soluble in cold ether, benzene, toluene, acetone and in hot acetic acid, ethyl, methyl and amyl alcohols. It is insoluble in water. Like all known aldazines it is a very stable compound.

2,4,6-Trimethylbenzyl-2,4,6-trimethylbenzal Hydrazone,

$$(CH_3)_3C_6H_2CH_2NHN : CHC_6H_2(CH_3)_3.$$

More than the calculated amount of a 4 per cent. sodium amalgam

[1] W. Graf: Inaug. Diss., Heidelberg, 1899.

to reduce the aldazine to its corresponding hydrazone was added to an alcoholic solution of 2,4,6-trimethylbenzaldazine. This was heated at the temperature of boiling alcohol in a flask connected with a reflux condenser for from four to five hours upon a water-bath. The almost colorless solution was then filtered and the filtrate placed in ice water. The hydrazone crystallized at once. It was filtered off, washed well with water and recrystallized from alcohol. It melted at 88°-89° (uncorr.).

The analysis gave 9.40 per cent. N. Calculated, 9.53 per cent.

2,4,6-Trimethylbenzyl-2,4,6-trimethylbenzal hydrazone is very soluble in ether and benzene, less soluble in acetic acid, ethyl and methyl alcohols and insoluble in water. It is very unstable, decomposing at once when exposed to the air and after a short time in an exhausted desiccator.

Acetyl 2,4,6-Dimethylbenzyl-2,4,6-trimethylbenzal Hydrazone,

$(CH_3)_3C_6H_2CH_2N(C_2H_3O)N : CHC_6H_2(CH_3)_3$.

To a concentrated alcoholic solution of the hydrazone was added acetic anhydride in excess and the solution evaporated slowly to dryness upon a water-bath. The residue was recrystallized from alcohol. Long, satin-like, white needles were formed which melted at 155°.

The analysis gave 8.42 per cent. N. Calculated, 8.34 per cent.

Acetyl 2,4,6-trimethylbenzyl-2,4,6,trimethylbenzal hydrazone is very soluble in chloroform, ether, benzene, toluene, acetic acid and acetone. It is less soluble in ethyl, methyl and amyl alcohols and insoluble in water. It is a very stable compound.

Benzoyl 2,4,6-Trimethylbenzyl-2,4,6-trimethylbenzal Hydrazone,

$(CH_3)_3C_6H_2CH_2N(C_7H_5O)N : CHC_6H_2(CH_3)_3$.

A slight excess of benzoyl chloride was added to a concentrated alcoholic solution of the hydrazone and the solution evaporated to dryness upon a water-bath. The residue was taken up and recrystallized from alcohol. Long, satin-like needles were formed which melted at 142.5°-143°.

The analysis gave 7.03 per cent. N. Calculated, 7.23 per cent.

The benzoyl derivative is very soluble in chloroform, ether, toluene, acetone, benzene and acetic acid. It is less soluble in ethyl, methyl, and amyl alcohols, and is insoluble in water. It is a very stable compound.

Nitroso 2,4,6-Trimethylbenzyl-2,4,6-trimethylbenzal Hydrazone, $(CH_3)_3C_6H_2CH_2N(NO)N : CHC_6H_2(CH_3)_3$.

To a strong alcoholic solution of 2,4,6-trimethylbenzyl-2,4,6-trimethylbenzal hydrazone, cooled by ice water, was added a few drops of concentrated hydrochloric acid. To this cold solution, which was shaken after each addition, was added gradually a concentrated solution of sodium nitrite. Long, satin-like needles separated at once and increased in number upon the addition of water. The successful carrying-out of this experiment requires the use of freshly prepared hydrazone.

The nitroso derivative was filtered off, washed well with water to remove the excess of sodium nitrite, and recrystallized from alcohol. The long, yellow, satin-like crystals melted at 117°.

The analysis gave 13.09 per cent. N. Calculated, 13.00 per cent.

The nitroso derivative is very soluble in chloroform, ether, benzene, and toluene. It is less soluble in acetone and glacial acetic acid. It is soluble in warm ethyl, methyl, and amyl alcohols, and insoluble in water. It is a stable compound.

UNIVERSITY OF MINNESOTA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

ARSENIC PENTACHLORIDE.

BY CHARLES BASKERVILLE AND H. H. BENNETT.

Received June 13, 1900.

THE non-existence of arsenic pentachloride has for a long time been regarded as remarkable, especially so when the analogues of that element having atomic weights below and above it, phosphorus and antimony, show pentavalence toward the halogens.

Hurtzig and Geuther[1] endeavored to prepare it by treating arsenious acid with phosphorus pentachloride. Mayerhofer[2] passed chlorine into arsenic trichloride at —10° C., removing the excess of chlorine by a stream of carbon dioxide, and failed to obtain the body. Janovsky[3] treated phosphorus pentachloride with arsenic trihydride at 0° C. with negative results. Dumas[4]

[1] *Ann. Chem. Pharm.*, 111, 171.
[2] *Ibid.*, 158, 326.
[3] *Ber. d. chem. Ges.*, 8, 1636 (1875).
[4] *Ann. Chem.* (Liebig), 33, 337.

thought he had arsenic pentachloride, but Capitaine[1] proved it to be a mixture of As_4O_6 and $AsCl_3$. Weber having prepared $SbCl_5PCl_5$, Cronander[2] sought its analogue $AsCl_5PCl_5$, but only obtained $AsCl_3PCl_5$. Marignac[3] obtained AsF_5 as a double fluoride of potassium. Sloane[4] prepared AsI_5 and endeavored to secure the pentachloride by saturating arsenic trichloride with chlorine at —23° C. at ordinary pressure and obtained the ratio As : Cl :: 1 : 4.447. There was a gradual decrease in the ratio up to 24° C. when it became 1 : 4.08, then there was an abrupt change rapidly approaching 1 : 3. Such observations made the existence of As_2Cl_8 quite conceivable.

Baeyer's pentahalogen compounds of arsenic in which one to four chlorine atoms have been replaced by alkyl radicals and Michaelis'[5] work with phenyl residues are well known. Recently the pentavalent organic arsenic compounds have become much augmented by the extensive work of Michaelis.[6]

The procedure of Sloane[7] offered encouragement, provided the reaction should be carried out at a lower temperature. Chemically pure arsenic trichloride was prepared and redistilled from concentrated sulphuric acid and its purity determined by analysis. About 5 cc. of the liquid were placed in a dry test-tube buried in solid carbon dioxide loosely packed in a Dewar bulb and dry chlorine led in. The crystalline trichloride (m. p. —18° C.) assumed a greenish yellow color and became liquid, which grew in bulk. Besson[8] showed that arsenic trichloride saturated with chlorine at zero does not solidify at —30° C. Davy also showed that it does not freeze at —29° C. when well saturated with chlorine. After a few minutes, the time varying with different experiments, the stream of gas was cut off and the excess of liquid chlorine removed by fractional distillation. Chlorine boils at —33.6° C. We verified this by completely boiling away several cubic centimeters of chlorine at —33° C. in other experiments. As a safeguard we allowed the temperature to rise to —31° C.

[1] *Jour. Pharm.*, 28, 524.
[2] *Ber. d. chem. Ges.*, 3, 1466 (1873).
[3] *Ann. Chem.* (Liebig), 145, 249.
[4] *Chem. News*, 46, 194 (1881).
[5] *Ber. d. chem. Ges.*, 8, 1316 and 9, 1566.
[6] *Ann. Chem.* (Liebig), 320, 271 (1902).
[7] *Loc. cit.*
[8] *Compt. rend.*, 109, 940.

The liquid was cooled again to —35° C. and samples were removed as the temperature rose by means of a small pipette chilled to the temperature of the refrigerating agent. These samples in one experiment were placed directly in water; in another it was deemed better to place them in a dilute sodium hydroxide solution. In the former case immediate solution occurred with those portions removed at temperatures below —25° C., while at those higher a white precipitate, evidently of arsenious oxide, formed, increasing in amount with elevation of temperature. The orthoarsenic acid was determined as magnesium pyroarsenate and chlorine as silver chloride. The filtrate from the magnesium ammonium arsenate in the former was tested for the presence of arsenious compounds. None were found up to —25° C., when arsenious acid was found in traces increasing in amount with rise of temperature. The ratio between arsenic as arsenic acid, and chlorine, was 1:5 or $AsCl_5$. At —25° C. the ratio rose to 1:6. The loss of chlorine and consequent return to the trivalent condition became more and more marked, the higher the temperature.

The following analytical results were obtained for two temperatures in one experiment:

Temperature. °C.	Amount taken.	Chlorine found. Per cent.	Theoretical.	Ratio obtained. As : Cl.
—35	0.1796	69.93	70.26	1 : 4.93
—25	0.26675	73.21		1 : 5.78

Arsenic pentachloride is readily soluble in carbon disulphide and absolute ether cooled to —30° C. From the latter, when chilled several degrees, it crystallizes in yellow prisms. It loses chlorine when heated above —28° C. On exposure to the air it fumes, evolving hydrochloric acid vapor and as the temperature rises forms crystals, most likely of the trichloride, which melt soon to the liquid state. A special preparation was made and sealed in a tube. The greenish-yellow liquid when cooled to —38° or —40° C. (we had no thermometer for determining this accurately) formed beautiful yellow crystals.

It is not regarded necessary to give our several unsuccessful preliminary experiments to secure the body for analysis. Suffice it to say that placing the body in a pipette or weighing-bottle at the temperature of the air brought about its immediate decomposition to the original trichloride, chlorine being evolved.

UNIVERSITY OF NORTH CAROLINA,
April 15, 1902.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 66.]

OBSERVATIONS ON THE ELECTROLYTIC PRECIPITATION OF ZINC AND OF COPPER.

BY EDGAR F. SMITH.

Received July 3, 1902.

THE suggestions made for the electrolytic determination of zinc are numerous. During the last few months the writer has had occasion to have some of them tried with the view of fixing the most advantageous working conditions, and in the course of this inquiry has noted what appears to him to be a matter of some analytical interest, *viz.*, that by employing as electrolyte a zinc salt solution containing an alkaline acetate very satisfactory results are obtainable in a comparatively brief period. It was Riché who first proposed this electrolyte, but it has not met with general use, perhaps because the proper working conditions were lacking. These are given in this communication. They have been repeatedly employed by different persons in this laboratory and have proved to be trustworthy. It was thought advisable, in the determinations made, to use as cathodes platinum dishes, upon the inner surface of which there was deposited a silver coating instead of one of copper.

WORKING CONDITIONS.

Potassium zinc sulphate	0.2002 gr. Zn.
Sodium acetate	1 gram.
Acetic acid (99 per cent.)	0.3 cc.
Total dilution	150 cc.
Cathode surface	100 sq. cm.
N.D.$_{100}$	0.36–0.70 ampere.
Voltage	4–5.
Temperature	65° C.
Time	2 hours.

A flat platinum spiral was used as anode. The solution was heated to the required temperature before the current was passed through it. At the beginning the pressure equaled four volts. This was maintained for an hour when it was increased to five volts, with the corresponding rise in amperage. On exposing a clean silver surface, if there was no further deposition of zinc and the liquid showed an acid reaction, a few drops of ammonia water were added to the point of neutralization and the action of the

current continued for about fifty minutes longer, after which a portion of the liquid was tested for zinc by the ferrocyanide method.

It will usually be noticed after an hour's action that the solution seems to be filled with bubbles. This is the proper time to introduce the ammonia water for neutralization. When the metal has been fully precipitated the liquid should be siphoned off, and the zinc deposit be washed with water, alcohol and ether. It may then be dried and weighed. By this procedure these results were obtained:

Zinc potassium sulphate. Grams.	Zinc found. Gram.	Zinc required. Gram.
1.3598	0.2006	0.2002
1.3580	0.1997	0.2000
1.2621	0.1806	0.1862
1.2742	0.1879	0.1883

The deposits of metal were all very adherent, free from sponginess and light gray in color.

Very often questions are asked regarding the availability of electrolytic methods in determining the quantities of metals in technical products. The idea seems to exist that these methods may be satisfactory enough and yield good results so long as pure salts or mixtures of the same are used, but that equal success will probably not be reached if natural products are used. Perhaps it would be well to try all proposed methods in this particular. The writer has no doubt in his own mind as to the outcome. It will be wholly satisfactory. Believing this he had several samples of zinc blende decomposed rapidly with acid, the solutions evaporated to dryness, the residues taken up in water and a drop or two of sulphuric acid, when the liquids were filtered and mixed with sodium acetate and a little free acetic acid, after which they were electrolyzed with conditions like those previously recorded. The results were as follows:

Zinc blende. Gram.	Zinc found. Gram.	Zinc. Per cent.
0.2523	0.1681	66.62
0.2497	0.1662	66.56

These values agree closely with those obtained by the ordinary gravimetric methods, but it need scarcely be mentioned that the

time-factor is very greatly reduced, so that this procedure will recommend itself. The point might be raised that blendes frequently contain iron; will it not contaminate the zinc? Such was not observed to be the case in any of the many determinations conducted in this way. Probably, if the quantity of iron present should be large there might serious doubt arise, but in all instances of that kind as the acetate solution is heated before the current is allowed to act, the basic iron acetate would appear, could be filtered out, and the solution then be treated as previously directed. The method surely deserves a thorough trial at the hands of analysts.

In this connection it may not be out of place to call attention to copper determinations in chalcopyrite made in the electrolytic way. This again is a natural product and with those who have felt uncertain how the copper determination by means of the current would result, it has been customary, after decomposition of the mineral, to precipitate the copper as sulphide, then dissolve it in nitric acid or in potassium cyanide and electrolyze. This is not necessary. After the mineral is decomposed, paying no attention to the sulphur, evaporate to dryness, take up the residue with a little sulphuric acid and water, and then proceed with the electrolysis, using such conditions as these:

Total dilution	150 cc.
Concentrated sulphuric acid	10 cc.
Temperature	60°–70°.
$N.D._{100}$	0.8–1.0 ampere.
Volts	2–3.
Time	1 hour, 30 minutes.

RESULTS.

Chalcopyrite. Gram.	Copper found. Gram.	Copper. Per cent.
0.2900	0.0963	33.20
0.2900	0.0969	33.41
0.5800	0.1932	33.31
0.5800	0.1936	33.37
0.5800	0.1936	33.37

The liquid siphoned off from the deposit of copper may be nearly neutralized with ammonia water and, after the introduction of ammonium oxalate, be electrolyzed at a temperature of 40°-65°, with a current of $N.D._{100} = 0.5$-1.0 ampere and 2-3.5 volts.

RESULTS.

Chalcopyrite. Gram.	Iron. Gram.	Iron. Per cent.
0.5800	0.1746	30.10
0.5800	0.1750	30.17

The question has been asked whether it is not possible, in a case like that of chalcopyrite, to render the original solution of the mineral ammoniacal and, not regarding the precipitated ferric hydrate, proceed with the electrolytic deposition of the copper. Many have felt that there was danger of iron entering into the deposit of copper, while others have declared that such a condition was not to be feared. During the past winter numerous tests of this question have been made in this laboratory, working with chalcopyrite. It has been found that if platinum dishes be employed as cathodes to receive the copper, the latter has invariably been contaminated with iron, but that if platinum cylinders, dipping into the ammoniacal solution contained in beaker-glasses, were used for cathodes the copper deposited upon them was free from iron.

The writer has had the assistance of Messrs. J. H. Graham and F. E. Walker in the experimental part of this study and would here acknowledge his indebtedness to them.

UNIVERSITY OF PENNSYLVANIA.

THE USE OF POTASSIUM-FERRIC CHLORIDE FOR THE SOLUTION OF STEEL IN MAKING THE DETERMINATION OF CARBON.

BY GEO. WM. SARGENT.

Received July 27, 1902.

THE reaction considered to take place when steel or iron drillings dissolve in potassium-cupric chloride is expressed thus:

$$Fe + CuCl_2 = FeCl_2 + Cu \text{ and } Cu + CuCl_2 = Cu_2Cl_2.$$

This result expressed without indicating the intermediate reaction is written as follows:

$$Fe + 2CuCl_2 = FeCl_2 + Cu_2Cl_2.$$

The solution takes place more quickly and without any loss of carbon if hydrochloric acid (sp. gr. 1.2) is present in the ratio of 1 cc. to 13 cc. of the double chloride solution. The above equations do not contain the potassium chloride since the part enacted

by it is not clearly understood; without it the drillings dissolve very much more slowly.

If instead of the copper salt, potassium-ferric chloride be used with just sufficient free hydrochloric acid present to prevent the separation of any basic iron salt, the drillings will be found to go into solution just as quickly and with no loss of carbon. The iron salt has the formula $FeCl_3,2KCl,H_2O$ and may be prepared by adding to a ferric chloride solution the requisite amount of potassium chloride and crystallizing out the double salt.

The chemically pure ferric chloride of commerce has the following composition:

	Per cent.
Ferric chloride	51.55
Hydrochloric acid	0.65
Water	48.80

If then to 267 grams of this commercial ferric chloride, 130.7 grams of potassium chloride are added and the whole, when dissolved in water, made up to 1 liter in volume, the resulting solution will be equivalent to the potassium-cupric chloride solution as usually prepared, except that it will contain free hydrochloric acid in the ratio of but 1 cc. to 225 cc. This amount is sufficient to prevent the formation of any basic salt and if this amount be much exceeded the acid will attack the drillings, giving off hydrogen and hydrocarbons. The reaction that takes place using the iron salt is analogous to that when the copper salt is used, leaving out of course the intermediate reaction, and is indicated by this equation:

$$Fe + 2FeCl_3 = 3FeCl_2.$$

If the solution is found to attack the drillings with evolution of hydrogen, the free hydrochloric acid must be neutralized until sufficient is left to just prevent the formation of basic salts of iron. The liquid should be a beautiful amber color when the conditions are perfect. As the drillings dissolve, the color becomes darker and of a greenish cast yet transparent so that when the solution of the drillings is complete, can more readily be ascertained than is the case when the copper salt is the solvent. The filtrate from the carbon is quite transparent, consequently whether the filtering medium has been a perfect one or not is quickly seen without the dilution of the filtrate as is required when potassium-cupric chloride is the decomposing agent.

This filtrate before it is contaminated with any wash-water, may be chlorinated and used again for the solution of a second lot of drillings. In this way, by chlorinating,[1] the filtrate from the carbon is made to decompose the next sample of drillings. When sufficient iron chloride has accumulated, add more potassium chloride and water to make the solution of the original strength. To illustrate, 200 cc. of the solution of $FeCl_2,2KCl$ containing about 50 grams of iron per liter are used in the decomposition of each factor weight, *2.7272* grams, of drillings. The liter will then contain besides the original amount 13.636 grams of iron. By chlorinating, four lots of 13.636 grams each or 54+ grams of iron may be dissolved in this liter. If 130.7 grams of potassium chloride be now added, the liter may be made two liters in volume. This operation of chlorinating, adding potassium chloride and diluting, may be carried on *ad infinitem*. It is, however, necessary at some point, determined by the amount of work done in the laboratory, to throw out a part of the accumulated solution.

In this way the waste product is utilized to assist in the next carbon determination and the expense materially reduced.

A table of results obtained by using both salts for the decomposition of the steels is appended.

Sample.	Dissolved in $CuCl_2,2KCl$. Per cent. carbon.	Dissolved in $FeCl_2,2KCl$. Per cent. carbon.
Standard 0.97 per cent	0.972	0.970
" 0.97 "	0.978	0.975
" 0.97 "	0.974	0.971
" 0.97 "	0.970	0.974
" 0.97 "	0.970	
" 0.97 "	0.968	
No. 5616	0.677	0.676
No. 5561	0.789	0.798
No. 5566	0.806	0.803
No. 5557	0.780	0.782
No. 4367 (a tungsten steel)	2.060	2.017
Standard 1.15 per cent	1.150	1.155
" 1.15 "	1.150	1.149
" 1.15 "	1.150	1.146
" 1.15 "	1.153	1.153
" 1.15 "	1.145	1.143
" 1.15 "		1.146

[1] This Journal, 22, 210.

It will be noticed that rather high carbon steels only have been dealt with and no irons. It is well known that mild steels and irons are more readily attacked by acid than high carbon steels. I have stated that the amount of free acid should not exceed 4.5 cc. per liter. This is a trifle more than sufficient to prevent any precipitation of basic iron salts, yet this solution, if allowed to stand upon a very mild steel or iron, will react with slight evolution of hydrogen. However if a very mild steel or iron be dissolved in this solution, the results vary from those obtained when the copper salt is the decomposing agent by amounts not exceeding the experimental error.

Sample.	Dissolved in $CuCl_2.2KCl$. Per cent. carbon.	Dissolved in $FeCl_3.2KCl$. Per cent. carbon.
No. 23943	0.383	0.388
No. 23943	0.375	0.383
Cast iron { combined carbon = 0.126 per cent. }	3.034	3.060

This would seem to indicate that the very dilute acid reacted upon the ferrite and not upon the cementite and that the carbon released from the Fe_3C by the $FeCl_3$ was not readily taken up by the hydrogen produced from the acid acting upon the ferrite. That cementite resists the action of acid is well known and is shown by the difficulty experienced in dissolving high carbon steel, also by the action of very dilute acid upon a polished specimen of a low carbon steel.

The action of light upon chlorine water is to produce hydrochloric acid and oxygen. Ferric chloride is also affected by the action of the light; hence it may be well to call attention to the fact that the chlorinated solution increases in acid content, particularly if it stands any length of time in the sunlight.

All the results obtaned in investigating the iron salt as a solvent have not been given, but sufficient to show that it can be used. The advantages derived from using it, especially where many determinations are made daily, will be apparent. The ease with which the point when all the drillings have gone into solution, is ascertained, the ready examination of the filtrate for any carbon that may have escaped the filter, and the economy recommend it.

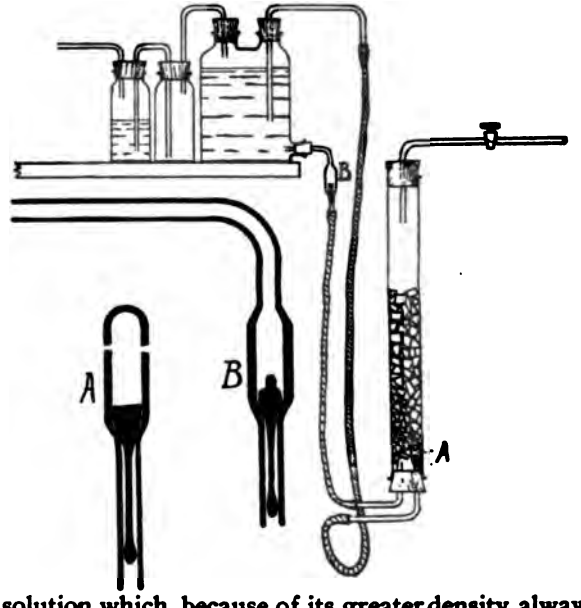
LABORATORY OF THE CARPENTER STEEL CO.,
READING, PA.

AN AUTOMATIC GAS-GENERATOR.

By Henry H. Denham.

Received August 2, 1900.

In the course of some experimental work recently begun the writer was confronted with the want of an automatic gas-generator which would yield at least a moderately steady supply of hydrogen sulphide without the necessity of frequent manipulation. As is well known, the Kipp and other forms of gas-generators in common use have the defect of using over and over the spent acid



and salt solution which, because of its greater density, always settles to the bottom of the apparatus. In order to use the whole of the acid it is consequently necessary to agitate the liquid from time to time. To the writer's knowledge there is but one form of automatic generator on the American market in which this necessity is obviated, and that is somewhat complicated.

With a somewhat limited supply of apparatus at hand, the following arrangement was devised which proved so satisfactory and practicable, and withal so simple of construction, that it seemed worth while to publish a description of it. In this description the dimensions are omitted, as it will readily be seen that the sizes of

the different parts will depend largely upon the gas to be prepared and the quantities in demand. The accompanying sketch will serve to show the general proportions of the apparatus in use in this laboratory.

A two-necked Woulff bottle, tubulated at the bottom, was used as an acid tank. The iron sulphide was contained in a glass tube, closed at its upper end with a one-hole rubber stopper fitted with a glass stop-cock, and at its lower end with a two-hole rubber stopper containing inlet and outlet tubes. The inlet tube terminates in a valve, *A*, opening upward just above the stopper, and is connected by rubber tubing to a glass tube passing through one neck of the acid bottle and terminating somewhat below the shoulder of the bottle. The outlet tube is open, and is connected by rubber tubing with another valve-tube, *B*, opening into the acid bottle through the tubulature at the bottom. The rubber tubes and the Woulff bottle being filled with dilute acid and the latter being placed at a suitable height above the generator, on opening the stop-cock, the acid enters the generator and the flow of gas commences at once. On closing the cock, the back pressure forces the acid from the generator back to the bottom of the acid bottle, and subsequent reopening allows the ingress of fresh acid into the generator. The second neck of the Woulff bottle was in this case connected with a trap for the absorption of any excess of hydrogen sulphide from the spent acid, and consisted merely of two bottles connected by glass tubing and containing a strong solution of potassium hydroxide. This would, of course, be unnecessary in many cases.

Separate sketches show the construction of the two valves, which will offer no difficulties to any one with slight skill in glass tube-working. The valves are simply glass rods of suitable size, drawn out and ground into their seats with turpentine, camphor and emery, before being cut from the long rod. Holes are drilled in the inlet valve-tube *A* by the use of the camphor mixture and a drill made from a round file. To guard against any possibility of the valve in *B* being carried upward by the current of liquid and consequently stopping the upper opening of the valve-tube, its top is pinched flat while still soft in the flame. Devices for washing and drying the gas are omitted from the drawing, as they would obviously vary with the gas and the use to which it was to be put.

BUFFALO CENTRAL HIGH SCHOOL,
July 19, 1902.

THE COPPER ASSAY BY THE IODIDE METHOD.

By Albert H. Low.

Received August 18, 1902.

From time to time the writer has seen statements reflecting on the accuracy of the iodide method for copper. The strictures are undoubtedly, in the main, perfectly just, according to the experience of their authors. When the writer first published his modification of the method, the preliminary experiments and the actual assaying of many ores seemed to justify all the statements then made. Continued use of the method, however, upon all kinds of material, eventually resulted in the discovery of slight inaccuracies under certain conditions not always recognized or understood at the time. Much attention has naturally been paid to the elimination of these troubles and apparently with success. As a result, the assay as now carried out in the writer's laboratory, while essentially the same as originally described, is nevertheless different in many of its details. It appears to leave but little to be desired on the score of accuracy and is perhaps of sufficient general interest to warrant publication.

DESCRIPTION OF THE METHOD.

Standardization of the Thiosulphate Solution.—Prepare a solution of sodium thiosulphate containing about 19 grams of the pure crystals to the liter. Standardize as follows: Weigh accurately about 0.200 gram of pure copper foil and place in a flask of about 250 cc. capacity. Dissolve by warming with 5 cc. of a mixture of equal volumes of strong nitric acid (sp. gr. 1.42) and water and then dilute to about 50 cc. Boil for a few moments to partially expel the red fumes and then add 5 cc. of strong bromine water and boil until the bromine is thoroughly expelled. The bromine is to ensure the complete destructon or removal of the red fumes. Remove from the heat and add a slight excess of strong ammonia water. Ordinarily it suffices to add 7 cc. of ammonia water of 0.90 sp. gr. Again boil until the excess of ammonia is expelled, as shown by a change of color of the liquid and a partial precipitation of the copper as hydroxide or oxide. Now add strong acetic acid in slight excess, perhaps 3 or 4 cc. of the 80 per cent. acid in all, and boil again for a moment if necessary to redissolve the

copper. Cool to room temperature and add about 3 grams of potassium iodide, or 6 cc. of a solution of the salt containing 50 grams in 100 cc. Cuprous iodide will be precipitated and iodine liberated according to the reaction

$$2(Cu.2C_2H_3O_2) + 4KI = Cu_2I_2 + 4(K.C_2H_3O_2) + 2I.$$

The free iodine colors the mixture brown. Titrate at once with the thiosulphate solution until the brown tinge has become weak and then add sufficient starch liquor to produce a marked blue coloration. Continue the titration cautiously until the color due to free iodine has entirely vanished. The blue color changes towards the end to a faint lilac. If at this point the thiosulphate be added drop by drop and a little time be allowed for complete reaction after each addition, there is no difficulty in hitting the end-point within a single drop. 1 cc. of the thiosulphate solution will be found to correspond to about 0.005 gram of copper, or about 1 per cent. in the case of an ore where 0.5 gram has been taken for assay. The reaction between the thiosulphate and the iodine is

$$2(Na_2S_2O_3) + 2I = 2NaI + Na_2S_4O_6.$$

Sodium iodide and tetrathionate are formed. The starch liquor may be made by boiling about 0.5 gram of starch with a little water and diluting with hot water to about 250 cc. The liquor should be homogeneous and free from lumps or grains. It should be used cold and must be prepared frequently, as it does not keep well. The thiosulphate solution made from the pure crystals and distilled water appears to be quite stable, showing little or no variation in a month under reasonable conditions.

Treatment of Ores.—To 0.5 gram of the ore in a flask of 250 cc. capacity add about 6 cc. of strong nitric acid and boil gently nearly to dryness. Then add 5 cc. of strong hydrochloric acid and again heat. As soon as the incrusted matter has dissolved add 6 cc. of strong sulphuric acid (sp. gr. 1.84) and boil until the more volatile acids are expelled and the fumes of sulphuric acid are coming off freely. This is best done over a naked flame. Allow to cool, add 25 cc. of cold water and heat the mixture to boiling. Allow to stand, hot, until any anhydrous ferric sulphate is entirely dissolved and then filter to remove more especially any lead sul-

phate. Receive the filtrate in a beaker about 6 cm. in diameter. Wash the flask and filter with either hot or cold water and make the volume of the filtrate about 75 cc. Place in the beaker a piece of sheet-aluminum prepared as follows: Cut a strip of stout sheet-aluminum 2.5 cm. wide and about 14 cm. long and bend this into a triangle so it will stand upon its edge in the beaker. The same aluminum may be used repeatedly as it is but little attacked each time. Add one large drop of a mixture of equal volumes of strong hydrochloric acid and water, cover the beaker and heat to boiling. Allow to boil from seven to ten minutes, which should be sufficient to precipitate all the copper in any case, provided the bulk of the solution does not much exceed 75 cc. Avoid boiling to a very small bulk, as, in that case, some of the precipitated copper may redissolve. The aluminum should now appear clean, the precipitated copper being detached or only loosely adhering. Remove from the heat and wash down the cover and sides of the beaker with cold water. There is danger of the finely divided copper being slightly oxidized and dissolved during the subsequent washing. To prevent this, and at the same time to precipitate any traces of copper still remaining in solution, add about 15 cc. of strong hydrogen sulphide water. If the copper in the ore does not much exceed 20 per cent. proceed as follows: Decant the supernatant liquid through a 9 cm. filter. Add 10 cc. of strong hydrogen sulphide water to the residue in the beaker and then transfer the liquid and precipitate to the filter. Wash thoroughly with cold water, without delay, to avoid oxidation. Now place the clean original flask under the funnel. Pour over the aluminum in the beaker 5 cc. of a mixture of equal volumes of strong nitric acid (sp. gr. 1.42) and water. Any adhering particles of copper will be thus dissolved. Heat to boiling but do not prolong the latter or the aluminum will be unnecessarily attacked. Pour the hot acid very slowly over the precipitate on the filter so as to dissolve all the copper, lifting the fold if necessary. Now, without washing, pour 5 cc. of a cold, saturated, aqueous solution of bromine into the filter and then wash the beaker and filter with hot water. Finally remove the filter and open it. If there remains a residue that might possibly contain copper it may be rinsed into the flask. The bromine has several functions. It cleanses the separated sulphur left on the

filter, it ensures the highest state of oxidation of any arsenic or antimony present, and it also effects the complete destruction or removal of the red fumes, which is a matter of great importance. If 5 cc. of bromine water are insufficient to impart a permanent tinge to the filtrate, more must be added. Boil the filtrate, which usually does not exceed 75 cc. in bulk, to thoroughly expel the excess of bromine, but avoid boiling to such a small bulk as to cause decomposition of bromides, etc. Remove from the heat and add ammonia water in slight excess (ordinarily 7 cc. of strong ammonia). Boil off the excess of ammonia, as shown by the change of color of the solution, and then acidify with acetic acid, again boiling if necessary to redissolve any precipitate containing copper. The addition of 3 or 4 cc. of the 80 per cent. acid is usually sufficient. A large excess of acetic acid does no harm but is not necessary except in the presence of sufficient arsenic to cause a precipitate of copper arsenate. This may require considerable acetic acid for its solution, perhaps 10 cc. If not mostly dissolved at this stage, it is taken up slowly later on and the titration may become very tedious before the true end-point is finally reached. Proceed with the acetic acid solution, after cooling to room temperature, precisely as described in the standardization of the thiosulphate and calculate the percentage of copper from the amount of the latter required.

In titrating low percentages of copper great care should be taken not to pass the end-point. Always work slowly towards the end and stop short of complete decolorization and then continue only when the liquid, after standing a minute or two, still persists in a tinge of color.

With high percentages it is usually advisable to wash the precipitated copper by decantation instead of on the filter. Proceed as follows: Transfer the liquid and copper in the beaker (to which hydrogen sulphide solution has been added) to the original flask and set the beaker and aluminum aside temporarily. Allow to settle, decant through the filter and wash the copper three or four times by decantation, the first time with hydrogen sulphide water and then with cold water, using about 20 cc. each time. Now place the flask and residue under the funnel, heat the 5 cc. of acid in the beaker as before and pour it through the filter. Do not add

the bromine for the moment but remove the flask, replacing it under the funnel with the beaker, and heat the acid until all the copper is dissolved and the red fumes are mostly expelled. Now return the flask under the funnel, add the bromine, proceed with the washing of the beaker and filter, and continue as described above.

Owing to the fact that the end-pont is somewhat sharper as the amount of copper present is less, the operator may perhaps find it advantageous in the case of very rich material to take only 0.25 gram instead of 0.5 gram for assay. As there seems to be no difficulty in doing accurate work by either plan, this is perhaps best left a matter of choice.

Notes.—According to the equation previously given, 0.5 gram of copper requires 2.62 grams potassium iodide. While direct experiment shows this to be apparently true, yet when only the theoretical amount of potassium iodide is present the reaction is slow and in fact does not appear to proceed to completion until during the titration, which is thereby unduly prolonged. It is best, therefore, to always use an excess, but as the iodide is expensive the quantity used should be governed by the amount of copper present, which can always be estimated approximately. Allow say 1 gram potassium iodide for every 15 per cent. copper, when 0.5 gram of ore is taken for assay. It is convenient to prepare a solution containing 50 grams of potassium iodide in 100 cc. A 2 cc. pipette will thus deliver 1 gram of the salt. No error will be introduced in a doubtful case by adding more potassium iodide after the titration is apparently finished and resuming the operation if the blue color is thereby restored.

Zinc and silver do not interfere with the assay. Lead and bismuth are without effect, except that by forming colored iodides they may mask the approach of the end-point before adding starch. Arsenic and antimony, when fully oxidized as described, have no influence. The return of the blue tinge in the titrated liquid after long standing is of no significance, but a quick return, which an additional drop or two of the thiosulphate does not permanently destroy, is usually an evidence of faulty work.

DENVER, COLORADO, August 14, 1902.

THE QUANTITATIVE DETERMINATION OF SELENIUM IN ORGANIC COMPOUNDS.

By R. E. Lyons and F. L. Shinn.

Received August 20, 1902.

The difficulties encountered in the estimation of selenium in organic compounds led to a study of the analytical methods in use. We have found these methods impracticable in their application tc selenium compounds which are to be decomposed with nitric acid. The results obtained were invariably too low.

It is stated in the literature,[1] and has been verified in this laboratory, that when metallic selenium is oxidized by nitric acid, the product is always selenious acid without a trace of selenic acid. This statement holds good in the case of organic compounds containing selenium when they are heated with red nitric acid in a sealed tube for several hours at temperatures between 180° and 260° C. Advantage has been taken of this deportment for the determination of selenium by methods based upon the reducibility of selenious acid by sulphur dioxide, hydrogen sulphide, sodium thiosulphate, hydriodic acid, etc.

The determination of selenium in solutions of selenious acid free from nitric acid is comparatively easy. Several of the methods proposed permit of a high degree of accuracy. The two following have best served our purpose:

(1) The old gravimetric method of Rose,[2] which consists in reducing the selenious acid, in the presence of hydrochloric acid, by means of sulphur dioxide, collecting the precipitate on a weighed paper, drying at 100° C., and weighing.

(2) The iodometric method of Norris and Fay,[3] whereby the selenious acid is reduced, in the presence of hydrochloric acid, by an excess of N/10 sodium thiosulphate solution and the excess determined by titrating back with a standard iodine solution.

Both methods when properly executed yield excellent results. The volumetric process is preferable when a number of estimations are to be made. It is simple, rapid and accurate.

Other methods deserving mention are those of Gooch and

[1] Wohlwill: *Ann. Chem. Pharm.*, 114, 173; Dammer: Band 1, 683; Roscoe and Schorlemmer: Vol. 1, 362.

[2] Pogg. *Ann.*, 113, 472; *Zischr. anal. Chem.*, 1, 73.

[3] *Am. Chem. J.*, 18, 703; 23, 119.

Pierce,[1] and Muthman and Schaeffer.[2] The latter method, however, has been studied by Gooch and Reynolds[3] and found to be inaccurate.

None of these methods are directly applicable to solutions of selenious acid containing free nitric acid, a condition obtaining from the customary oxidation of selenium and its compounds with nitric acid. To free such solutions from nitric acid without loss of selenium has afforded great difficulty from the time of the first attempts to estimate this metal.

Rose[4] states that solutions of selenious acid can not be heated above 100° C. without volatilization of selenium dioxide and provides for the removal of the nitric acid by evaporation on a water-bath. It has been our experience, and the experience of others, that with the most carefully conducted evaporations a loss of selenium invariably occurs.

Divers and Schimose[5] attribute the low results to the formation of selenic acid during the evaporation with nitric acid. They recommend boiling the residue with hydrochloric acid for the purpose of reducing any selenic acid to selenious acid. This precaution is manifestly unnecessary when nitric acid alone has been used to decompose the compound.

Rathke[6] recommended the addition of hydrochloric acid to the selenious acid solution previous to evaporation. Later,[7] he suggested the addition of sodium or potassium chloride to the solution to prevent volatilization of selenium chloride during the repeated evaporations with hydrochloric acid. The results of Rathke's analyses show a loss of from 1 to 5 per cent.

Michaelis,[8] finding that evaporation with hydrochloric acid always resulted in the loss of selenium, sought to avoid evaporation by boiling the solution with a great excess of concentrated hydrochloric acid until the nitric acid should be completely decomposed. The operation was conducted in a flask provided with a return condenser. Michaelis used this scheme success-

[1] *Am. J. Sci.*, 1, (4), 31.
[2] *Ber. d. chem. Ges*, 26, 1008.
[3] *Am. J. Sci.*, 30, 254.
[4] *Ztschr. anal. Chem.*, 1, 73.
[5] *J. Chem. Soc.*, 57, 439.
[6] *Ann. Chem. Pharm.*, 152, 194 and 206.
[7] *J. prakt. Chem.*, 108, 249.
[8] *Ber. d. chem. Ges.*, 30, 2827.

fully, in connection with the gravimetric method, when ordinary nitric acid was employed to bring about the decomposition of the organic compound. It is our experience that when as little as 4 or 5 cc. of red fuming nitric acid are used, several hours' boiling under an inverted cooler is not sufficient to bring about complete decomposition and removal of the nitric acid. The method, even should it be successful, is a very great time-consumer and is troublesome from a mechanical standpoint. Further, the solution of selenious acid so treated would be unfit for direct titration, according to the method of Norris and Fay, on account of the large and unknown amount of hydrochloric acid present. It has been demonstrated that for accurate results with the method of Norris and Fay the amount of hydrochloric acid employed must fall within a certain, well-defined limit.[1]

The method suggested in this paper for the elimination of the nitric acid has the advantage of easy execution, requires less time and attention, and gives very accurate results when used in connection with either the gravimetric or volumetric methods for determining the selenium in solutions of selenious acid.

In the attempted estimations of selenium in a number of compounds, some of which contained mercury, we observed that in the case of a mercuric chloride compound the results always came nearer the theoretical than was true with the purely organic compounds. This deportment is verified in the analytical results reported by Rathke.[2] In a body, $C_3H_5Se_2OK$, the selenium found was 58.21 per cent. (theory 62.36 per cent.), while in the compound $2Se(C_2H_5)_3Cl + ZnCl_2$, containing the heavy metal zinc, the selenium found was 28.59 per cent. (theory 29.44 per cent.).

The plausible explanation of this deportment is that the heavy metal present forms with the selenious acid a selenite which is stable at the temperature of the water-bath, thus retaining all of the selenious acid in combination during the evaporation.

Accordingly, exactly equivalent portions of mercuric nitrate were weighed out and dissolved in the selenious acid solution previous to evaporation. The results were encouraging rather than satisfactory. The quantity of selenium usually lost by

[1] Norton: *Am. J. Sci.*, 137, 287; Norris and Fay: *Am. Chem. J.*, 23, 123.

[2] *Ann. Chem. Pharm.*, 152, 207-212.

evaporation in the absence of a heavy metal was found much diminished. It would be impracticable, for obvious reasons, to have in the solution always a quantity of mercury salt exactly equivalent to the selenious acid. It became evident that the metal added to the solution to retain the selenious acid during the evaporation must form a selenite perfectly stable at 100° C., and sufficiently insoluble in cold water to permit of washing free from nitrates and nitric acid. A number of simple selenites, *e. g.*, cadmium, mercury, magnesium and silver, were tried but without success. All were found too soluble for quantitative purposes. A further search in the literature was rewarded by finding the statement of Boutzoureano[1] concerning the double selenite ammonia compounds. A number of selenites dissolve in ammonium hydroxide and upon evaporation of the solution on a water-bath, or in a vacuum, form double compounds, *e. g.*, $Ag_2SeO_3NH_3$. Silver and zinc selenite ammonia may be formed in this way. These compounds are insoluble in water, soluble in acids and perfectly stable at 100° C.

It was foreseen from this, that if to a solution of selenious acid containing nitric acid an excess of silver or zinc nitrate be added and the solution evaporated to dryness to expel the nitric acid, the residue, containing all of the selenium as selenite, could then be evaporated with ammonium hydroxide to form the double selenite ammonia. This compound, it was hoped, would permit of washing free from nitrates without appreciable loss. The residue of silver or zinc selenite ammonia could then be decomposed by means of hydrochloric acid, and the usual gravimetric or volumetric methods for the estimation of selenious acid applied. The method was tried and proved entirely successful.

EXPERIMENTAL PART.

Preparation of Pure Selenium Dioxide.—Pulverized selenium was oxidized with concentrated nitric acid and the reaction mixture evaporated to dryness on a water-bath. The residue was moistened with nitric acid and sublimed in a small beaker according to the method suggested by Norris and Fay.[2] To ensure greater purity the above product was resublimed in a current of

[1] *Jahresb. u. Fortschritte d. Chem.*, 42, 390.
[2] *Am. Chem. J.*, 18, 704.

dry oxygen in a combustion tube. The selenium dioxide so obtained, in the form of delicate, white needles, was dried to constant weight in a vacuum desiccator over phosphorus pentoxide. An accurately weighed quantity of pure selenium dioxide was dissolved in water, the solution acidulated with a drop of concentrated hydrochloric acid and diluted to 1000 cc.

In all of the following experiments the volumetric method of Norris and Fay[1] was used for the final estimation of the selenious acid.

Direct Titration of the Selenious Acid Solution.—Portions of the selenious acid solution, 25 cc. each, were titrated directly with the following result:

	Selenium present. Gram.	N/10 $Na_2S_2O_3$ used. cc.	Selenium found. Gram.
(*a*)	0.05468	27.69	0.05469
(*b*)	0.05468	27.63	0.05457
(*c*)	0.05468	27.65	0.05461

Determination of Selenium in Solutions Containing Nitric Acid.—(*a*) Portions of 25 cc. of the selenious acid solution were treated with a slight excess of silver nitrate and about 2 cc. of fuming nitric acid. The evaporation to dryness and repeated treatment with ammonium hydroxide was then carried out according to the method to be described later. Following are the results:

	Selenium present. Gram.	N/10 $Na_2S_2O_3$ used. cc.	Selenium found. Gram.
(*a*)	0.05468	27.83	0.05498
(*b*)	0.06491	32.78	0.06472
(*c*)	0.06491	32.88	0.06489
(*d*)	0.06491	32.75	0.06468
(*e*)	0.06491	32.77	0.06470

(*b*) An excess of zinc nitrate was used instead of silver nitrate in a series of experiments similar to (*a*), with the following result:

	Selenium present. Gram.	N/10 $Na_2S_2O_3$ used. cc.	Selenium found. Gram.
(*a*)	0.06491	32.71	0.06460
(*b*)	0.06491	32.75	0.06468

(*c*) Similar experiments were made using cadmium nitrate in place of silver or zinc nitrate. The results were very much too low. Cadmium selenite ammonia, $CdSeO_3.NH_3$, does not withstand the washing.

[1] *Am. Chem. J.*, 18, 704; 23, 119.

(*d*) The selenium in the following aromatic selenium compounds was determined by this process:

	Weight of substance.[1]	Evaporated with zinc or silver nitrate.	N/10 $Na_2S_2O_3$ used. cc.	Se present.	Se found.	Theory. Per cent.	Found. Per cent.
(1)	0.10745	$AgNO_3$	27.52	0.05444	0.05436	50.67	50.59
(2)	0.21445	$Zn(NO_3)_2$	54.78	0.10866	0.10819	50.67	50.46
(3)	0.09065	$AgNO_3$	21.23	0.04212	0.04193	46.47	46.25
(4)	0.0945	$AgNO_3$	14.84	0.02950	0.02931	31.22	31.01

We recommend the following procedure for the determination of selenium in organic compounds:

Heat a weighed quantity of the substance in a sealed tube with red fuming nitric acid one hour, or longer, at a temperature of 235° or 240° C. Transfer the contents of the tube, together with the wash-water, to an evaporating dish of about 400 cc. capacity. Add about 1/4 more silver or zinc nitrate than is theoretically required to unite with the selenious acid present. Evaporate to dryness on a water-bath.[2] Wash down the sides of the dish with a little water and again evaporate to dryness. Treat the residue twice with about 50 cc. dilute ammonium hydroxide and evaporate after each addition. Add water and evaporate twice to ensure complete removal of free ammonia. When cool, wash the residue with water, decanting the wash-water on a filter, until free from nitrates. Place the filter-paper in the evaporating dish, decompose the silver or zinc selenite ammonia with 10 cc. hydrochloric acid (sp. gr. 1.124), dilute the solution to about 300 cc. with water and add a few pieces of ice.

Run in N/10 sodium thiosulphate solution in slight excess,[3] allow the mixture to stand one hour[4] and determine the excess of thiosulphate by titration with standard iodine solution.

1 cc. N/10 $Na_2S_2O_3$ solution = 0.001975 gram of metallic selenium.

To estimate the selenium gravimetrically:

(*a*) In case silver nitrate is used: Filter after decomposing the

[1] The substance used in (1) and (2) is di-phenyl-di-selenide; in (3) di-benzyl-di-selenide; and in (4) a compound, $C_{27}H_{24}Se_2$.

[2] The water-bath must not be allowed to go dry during this or any subsequent evaporation.

[3] We have found this method most accurate when the excess of N/10 thiosulphate employed does not exceed 5 to 7 cc. Compare Norton: *Am. J. Sci.*, 137, 287; also Norris and Fay: *Am. Chem. J.*, 23, 123.

[4] The mixture must be kept near the temperature of melting ice during the reduction with thiosulphate.

silver selenite ammonia with hydrochloric acid, wash the paper free from chlorine and reduce the selenious acid in the filtrate by means of sodium bisulphite.

(*b*) In case zinc nitrate is used: Filtering after the decomposition with hydrochloric acid may be omitted.

INDIANA UNIVERSITY, BLOOMINGTON, IND.,
August, 1902.

[CONTRIBUTION FROM THE LABORATORY OF THE PENNSYLVANIA STATE COLLEGE EXPERIMENT STATION.]

THE DETERMINATION OF SULPHUR AND PHOSPHORUS IN PLANT SUBSTANCES.

BY C. P. BRISTLE.

Received September 3, 1902.

IT IS commonly known to chemists that plant materials, in their conversion to ash by burning, lose not only water, carbon dioxide, and nitrogen as the gaseous products of their ignition, but generally some portion of their sulphur and phosphorus as well.[1] Experience of other analysts has shown that such losses can not be avoided, like those of alkaline chlorides, by any simple precaution. The accurate determination of sulphur and phosphorus is of great importance in calculating the heat of combustion in plant substances from their elementary analysis, and the determination of phosphorus in estimating the soil-exhausting action of vegetable products. The ordinary ash analysis is insufficient for such purposes.

The following work was undertaken at the suggestion and under the direction of Dr. William Frear. The determination of sulphur and phosphorus in plant substances is carried on by a number of different methods and a comparison of results on a few of these methods is all that was attempted. The substances analyzed were cottonseed-meal and timothy hay. There were also a few determinations made on egg albumen. These substances were chosen on account of the wide difference in their sulphur and phosphorus content, the cottonseed-meal containing relatively large amounts, while the timothy hay is very poor in these elements. The methods used were as follows:

[1] Wiley's "Principles and Practice of Agricultural Analysis," Vol. I. pp. 419-420; Vol. III. pp. 37, 430 and 446.

First. Determination of the sulphur and phosphoric acid in the ashes of the substances.—About 5 or 10 grams of the sample were incinerated in a platinum dish; the ash was digested with a little dilute hydrochloric acid and then washed on a filter with hot water. The filtrate and washings were made up to about 150 cc. and then, while hot, barium chloride solution was added. After standing twelve hours, the solution was filtered, and the barium sulphate was washed, ignited, and weighed; the amount of sulphur was calculated from the weight of barium sulphate. The filtrate and washings from the barium sulphate precipitation were evaporated to a small bulk, the hydrochloric acid neutralized with ammonia and the solution was acidified with nitric acid. Phosphoric acid was then determined in the usual way with ammonium molybdate and magnesia mixture.

Second. Destruction of organic matter by fusion with potassium hydroxide and nitrate and determination of sulphur and phosphoric acid in the fused mass.—Two grams of the sample were fused with a mixture of 20 grams of potassium hydroxide and 6 or 8 grams of potassium nitrate. The fusion was made in platinum crucibles heated by gasoline gas. Blank determinations were made, which gave no trace of sulphur or phosphorus, showing both the purity of the reagents used, and that no sulphur was absorbed from the gas. After complete fusion was obtained the mass was cooled, dissolved in hot water, and then carefully acidified with hydrochloric acid. Sulphur and phosphoric acid were determined in this solution as before. A blank determination was made on the potassium hydroxide and potassium nitrate but neither sulphur nor phosphoric acid was found.

Third. Destruction of organic matter by action of potassium hydroxide followed by chlorine, and determination of sulphur and phosphoric acid in residues.—Two grams of the sample were boiled with about 200 cc. of a strong potassium hydroxide solution for thirty minutes. Chlorine was then passed through the solution till it was decolorized. The solution was then acidified with hydrochloric acid and filtered. The sulphur and phosphoric acid in the solution were determined in the usual way.

Fourth. Destruction of organic matter by ignition with oxygen in a bomb-calorimeter and determination of the sulphur and phos-

phoric acid in the products of combustion.—A 2-gram sample was pressed into a small tablet and placed in a Hempel-Atwater bomb-calorimeter. The bomb was then filled with oxygen at a pressure of 18 atmospheres. The sample was ignited by an electric fuse. During combustion, the bomb was surrounded by cold water, as is usual in determining heats of combustion, and kept thus cooled for fifteen minutes, so that the condensation of the vapors formed in the bomb might be as complete as possible. Owing to the high pressure of the gases enclosed within the bomb and the nature of its vent, the regulation of their escape, in such manner as to ensure the complete absorption of any substances containing sulphur or phosphorus that might have escaped condensation, seemed impossible. The method is, therefore, valid only in so far as the sulphur and phosphoric acid are retained in the solid and liquid residues within the bomb. The liquid contained only traces of phosphoric acid; this constituent appearing chiefly in the solid residues. After the ignition, the bomb was opened, the liquid it contained was washed into a beaker and the small amount of ash, which was usually in the form of an insoluble glassy slag, was fused with sodium carbonate. This fusion was dissolved in hot water, and the solution added to the liquid washed from the inside of the bomb. The sulphur and phosphoric acid were then determined in the solution.

Fifth. Destruction of organic matter by a boiling mixture of nitric and hydrochloric acids, and determination of sulphur and phosphoric acid in the resulting solution.—The samples were treated according to the method of the Association of Official Agricultural Chemists for total phosphoric acid. Two grams of the sample were boiled for thirty minutes in a mixture of nitric and hydrochloric acids. The sulphur and phosphoric acid were determined in the solution. In some of the determinations on cottonseed-meal the boiling was carried on for a much longer time and the acid lost by evaporation was replaced by more acid.

Sixth. Destruction of organic matter by burning in oxygen in a combustion tube and determination of sulphur and phosphoric acid both in the residual and escaping gases.—The sample was burned in a combustion tube in a current of oxygen. The products of combustion were passed through a series of absorption tubes

containing a hydrochloric acid solution of bromine. After the combustion was completed, the solution in the absorption tubes was emptied into a beaker. The combustion tube was washed out to remove the ash, and the washings were added to the solution from absorption tubes. The mixed solutions were boiled till all the bromine was expelled, and then filtered. The sulphuric acid was then determined in the clear solution as usual. The complete combustion of the organic matter was attained with difficulty; undecomposed vapors tended to form a tarry deposit at the exit end of the tube; this was finally overcome, first, by introducing the oxygen not only at the end of the combustion tube, but also, by means of a small tube inserted at a point about an inch beyond the boat containing the burning material; and, second, by taking pains to keep the tube at a bright red heat for a few inches beyond the entrance of the second stream of oxygen. With these precautions, no condensaton of tarry products occurred. To secure the most complete contact of the escaping gases with the bromine solution, the latter was held in four 6-inch, 3-bulb U-tubes set in a pan of cool water, and the gases were evolved slowly as in a carbon determination.

Seventh. Ignition after saturation with a solution of calcium acetate.—The sulphur was also determined according to a modification of the method proposed by A. E. Shuttleworth of Ontario Agricultural College. Ten grams of the sample were saturated with 20 cc. of a solution of calcium acetate containing 29.2 grams to the liter. The material was then incinerated and sulphur determined in the ash. These incinerations took place in a platinum crucible.

Eighth. Ignition after saturation with a solution of barium hydroxide.—Ten grams of the cottonseed-meal were saturated with a solution of barium hydroxide, dried, and ignited. The ash was fused with sodium carbonate, the fused mass extracted with hot water, the solution filtered and the sulphur determined in the filtrate as usual.

A partial analysis of the organic substances used, was made with the following results:

TABLE I.—FODDER ANALYSIS OF MATERIALS.

	Moisture.		Fat.		Protein.[1]	Ash.	
Cottonseed-meal ..	7.08	7.13	10.05	10.00	42.12	5.73	5.70
Timothy hay	4.55	4.50	2.02	2.02	4.75	3.81	3.84
Egg white (dry)..	...	...	...	...	83.37	6.02	...

As previous statements indicate, the results are somewhat differently expressed for the two elements under consideration, those for sulphur being given in terms of the element itself, those for phosphorus in terms of the pentoxide, P_2O_5, commonly spoken of, in agricultural chemical literature, as "phosphoric acid". The reason for the distinction is that evidence points to the existence of phosphorus in plants principally in the form of phosphoric acid, except in the seeds where it exists largely in the organic form in lecithins and other similar compounds; and to the fact that sulphur is present principally in some other state of combination than sulphuric acid.

The following experiment clearly shows this fact. Any sulphates present in a plant substance can be removed by careful extraction with hydrochloric acid of moderate strength and can be precipitated from the solution directly. The cottonseed-meal was thus extracted with acid of 1.06 sp. gr.; the solution contained sulphuric acid (SO_3) equivalent to 0.159 per cent. of the meal (as the result of duplicate, exactly concordant determinations); this corresponds to 0.064 per cent. of sulphur, about one-ninth of all the sulphur present.

The results of the several determinations of sulphur and phosphoric acid in cottonseed-meal and timothy hay by the foregoing eight methods are presented in Tables II-IV.

TABLE II.—SULPHUR.

Methods.	Cottonseed-meal. I. Per cent.	Cottonseed-meal. II. Per cent.		Timothy hay. I. Per cent.	Timothy hay. II. Per cent.
1. In ash	0.046	0.040		0.048	0.042
2. Fusion with potassium hydroxide and nitrate	0.570	0.550		0.145	0.135
3. Destruction by potassium hydroxide and chlorine	0.280	0.280			
4. In bomb-calorimeter products	0.440	0.410		0.075	0.068
5. In solution with hydrochloric and nitric acids	0.230	0.240			
	0.220[2]	0.230[2]			

[1] Nitrogen × 6.25.

[2] After extraction with ether.

Methods.	Cottonseed-meal. I. Per cent.	Cottonseed-meal. II. Per cent.		Timothy hay. I. Per cent.	Timothy hay. II. Per cent.
6. In products of ignition in combustion tube	0.470	0.440	0.450		
7. Ignition after saturation with calcium acetate	0.120	0.120		0.044	0.044
8. Ignition after saturation with barium hydroxide	0.065	0.070			

TABLE III.—PHOSPHORIC ACID.

Methods.	Cottonseed-meal. I. Per cent.	Cottonseed-meal. II. Per cent.	Timothy hay. I. Per cent.	Timothy hay. II. Per cent.	Timothy hay. III. Per cent.
1. In ash	2.41	2.31	0.355	0.345	...
2. Fusion with potassium hydroxide and nitrate	2.51	2.45	0.34	0.32	...
3. Destruction by potassium hydroxide and chlorine	0.42	0.46	...	...	...
4. In bomb-calorimeter products	2.21	2.34	0.29	0.29	...
5. In solution with hydrochloric and nitric acids	1.33	1.33	0.35	0.36	0.32
6. In products of ignition in combustion tube	0.78[1]	0.73[1]	...	...	...

[1] After extraction with ether.

TABLE IV.—ANALYSIS OF EGG ALBUMEN.

Method.	Calculated to dry substance. Sulphur.	Phosphoric acid.
1. In ash	0.196	0.21
2. Fusion with potassium hydroxide and nitrate	1.60	0.22

Sulphur.—It will be seen from these results that the fusion with potassium hydroxide and potassium nitrate gave the highest results for sulphur in all three of the substances examined, and that this method gave results on sulphur in egg albumen closely coinciding with those found by Hoppe-Seyler in the same substance; *viz.*, 1.57 per cent. The amount of sulphur in the ash of the various samples is so low that it gives no indication of the total amount of sulphur present, showing that the greater portion is driven off by ignition. The sulphur obtained by boiling with potassium hydroxide solution, with subsequent oxidation with chlorine, gave only half the sulphur found by the fusion method. The sulphur found by ignition in the bomb-calorimeter is about the same in amount as that found by combustion in a stream of oxygen and absorption of the products of combustion in a hydrochloric acid solution of bromine, but is still considerably less than

is obtained by fusion.[1] It seemed to be impossible to completely oxidize and fix all the sulphur by any other method than by fusion with alkaline nitrate. The methods of saturating the substance with barium hydroxide solution and calcium acetate solution, respectively, before ignition, give results considerably higher than simple incineration without previous saturation; still, they are so far below those given by other methods that they are of slight value.

The great difficulty in the determination of sulphur in organic substances is to get all the sulphur completely oxidized. This was shown by the fact that when cottonseed-meal was fused with potassium hydroxide without enough nitrate being added to completely burn up the organic matter, the results were too low; also, the fusion thus obtained gave off hydrogen sulphide gas when treated with hydrochloric acid, showing that part of the sulphur had been fixed by the alkali but not oxidized.

Phosphoric Acid.—The fusion method gave slightly more phosphoric acid than the ash in the case of the cottonseed-meal, but practically the same for the timothy hay and egg albumen. This would indicate that in the substances examined, the phosphoric acid was volatile to a very slight extent if it all. Boiling with potassium hydroxide solution and treating with chlorine gave results so low, that this method may be discarded for the analysis of this class of bodies. The phosphoric acid found by ignition in the bomb-calorimeter was slightly less than by fusion, and this difference was probably due to mechanical loss of the smaller particles of the glassy slag which contained almost all the phosphoric acid.

The amount of phosphoric acid obtained from the hay by boiling with nitrohydrochloric acid was practically the same as found by fusion or incineration. When the cottonseed-meal was treated in this way only about half of the phosphoric acid present was obtained. It was thought at first that the phosphoric acid had not been taken into solution. When a sample of the cottonseed-meal was placed on a paper filter and extracted with nitric acid (sp. gr. 1.15), the phosphoric acid determined in the filtrate by direct precipitation amounted to 0.16 per cent. Other samples were treated as above, except that the filtrate was evaporated to dryness, the residue ignited, cooled, and then dissolved in nitrohydrochloric

[1] [See, however, the following article. EDITOR.]

acid. The phosphoric acid was determined in the resultant solution, and in three determinations the results were respectively 2.18, 2.22, and 2.31 per cent. This shows that the phosphoric acid was readily taken into solution by the action of nitrohydrochloric acid on the seed meal, but in such form that it could not be entirely precipitated by ammonium molybdate till after ignition and subsequent solution in nitric acid. Work done by Hardin[1] indicates the presence of meta- and pyrophosphoric acid in cottonseed-meal; but these forms of phosphoric acid should be converted into orthophosphoric acid by boiling with strong nitric acid.

Possibly the phosphoric acid in cottonseed-meal is in organic combination that is not broken up by boiling with strong nitrohydrochloric acid and can only be set free by ignition or fusion.

The cottonseed-meal was extracted with anhydrous ether, and the ether extract was fused with potassium hydrodixe and potassium nitrate and the sulphur and phosphorus determined. The extract contained 0.47 per cent. phosphorus pentoxide, probably contained in ether-soluble lecithins; most of the phosphorus in these compounds is driven off by ignition and this would account for some of the difference in results between the methods of fusion with alkali and simple ignition.

The sulphur obtained from the ether extract by the fusion method amounted to 0.30 per cent. of the extract, or calculated to original substance, 0.03 per cent.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 71.]

THE DETERMINATION OF SULPHUR AND PHOSPHORUS IN ORGANIC MATERIALS.

BY H. C. SHERMAN.

Received September 17, 1902.

THE DETERMINATION OF SULPHUR.

IN order to secure complete oxidation of the sulphur of organic materials without loss through the formation of volatile compounds a great many modes of procedure have been described. Without attempting an enumeration of these it may be said that nearly all of them fall under one of three general heads:

[1] Bulletin 35 U. S. Dept. of Agriculture, Division of Chemistry, p. 50.

(1) oxidation by means of nitric acid in a sealed tube; (2) heating in a combustion tube in a current of air, oxygen or some oxidizing vapor—the oxidation being sometimes completed by means of platinized asbestos; (3) fusion with an alkali (sometimes with previous treatment with nitric acid), the oxidation being completed either by the addition of an oxidizing agent to the fusion or by treating the alkaline solution with chlorine or bromine. The first method is quite inconvenient for samples low in sulphur because only small amounts of material can be decomposed at a time and determinations are frequently lost through breaking of the tubes. The second method requires the fitting up of special apparatus and is not apt to be used unless many determinations are required. Hence some modification of the third general method is apt to be preferred and the most common is perhaps the fusion of the substance with sodium hydroxide with the addition of nitrate or peroxide to complete the oxidation. This method, if carefully carried out, can be made to yield very accurate results, at least with ordinary materials, but it appears that equally accurate results can be more conveniently obtained by direct combustion in oxygen.

Berthelot in 1892[1] proposed the use of the calorimetric bomb for the elementary analysis of organic substances and stated that on combustion with 25 atmospheres of oxygen the sulphur, as well as the carbon and hydrogen, was completely oxidized, and in the presence of moisture remained entirely in the form of sulphuric acid. This method has been used to some extent, especially for the determination of sulphur in coals, and Hempel has described[2] a modification in which the combustion is accomplished in a large glass vessel with oxygen at ordinary pressure.

As an additional precaution the gases from the bomb after the combustion may be made to pass through bromine water to which the rinsings of the combustion chamber may afterwards be added and the whole boiled to insure the oxidation of any sulphurous acid which may have been formed. This is considered unnecessary by Hempel and the following experiments show that the bromine was not needed with the samples here used: Dried meat, dried curd and white of egg were burned and the sulphur deter-

[1] *Compt. rend.*, 114, 317, 318.

[2] *Ztschr. angew. Chem.* (1892), pp. 393-394.

mined as described below with the additional precaution of the use of bromine as just mentioned. The same samples were then treated in exactly the same way except that the wash-bottle through which the escaping gases passed contained only water, which was subsequently used for rinsing out the combustion chamber. After passing through the water the escaping gases were led through a second wash-bottle containing bromine water. The same portion of bromine water was used for these three combustions and was then examined and found to have absorbed no sulphur. The results with and without the use of bromine were as follows:

	Percentage of sulphur found.	
	Using bromine water.	Using water only.
Dried lean meat	0.814	0.816
Dried curd	0.611	0.609
Dried white of egg	1.406	1.410

These tests seemed to show conclusively that for these samples the use of bromine was entirely unnecessary and in the subsequent use of this method we have carried it out as follows:

Compressed Oxygen Method.—A suitable amount of sample is pressed into a pellet and burned in the bomb-calorimeter[1] in the same manner as in the determination of heat of combustion, using from 25 to 30 atmospheres of oxygen. By means of a coupling with small bore the bomb is then connected with a wash-bottle containing water, and the gas is allowed to bubble through the water until the contents of the bomb reaches atmospheric pressure, when it is opened and thoroughly rinsed with water. In order to keep down the volume, the water from the wash-bottle is used for the first rinsing. Any ash found in the combustion capsule is dissolved by means of hydrochloric acid and this solution added to the main solution. The whole is then boiled down to the desired volume, filtered if necessary, and the sulphuric acid determined by precipitation with barium chloride.

This method has been applied to a few sulphur compounds prepared by students in the organic laboratory, selecting such as contained sulphur in an "unoxidized" condition in order to make the test as decisive as possible. The following results were obtained:

[1] In these experiments a platinum-lined Atwater-Blakeslee bomb was used.

	Percentage of sulphur.	
	Theoretical.	Found.
Benzyl sulphocyanide	21.49	21.52
Benzyl sulphide	14.96	14.77
Diphenyl thiourea	14.04	13.85
Benzyl sulphoxide	13.92	13.72

The oxygen method was then compared with the alkali method, using sodium peroxide as the oxidizing agent and with the "nitric acid method" as provisionally adopted for the determination of sulphur in plants at the last (1901) meeting of the Association of Official Agricultural Chemists.

Alkali Method.—This was carried out essentially as described by Osborne.[1] Fifteen grams of sodium peroxide were weighed and most of it introduced at once into a large silver crucible and converted into hydroxide by adding a little water and boiling over an alcohol lamp until the excess of water was expelled. The hydroxide was allowed to cool until pasty when the sample was added and stirred into the alkali as quickly as possible. The heat was then gradually raised and the remainder of the peroxide added in small portions to complete the oxidation. The fused mass was then allowed to cool, was dissolved and washed into a beaker with water,[2] acidulated with hydrochloric acid and boiled. Finally the solution was filtered, neutralized with ammonia, brought to the desired volume and acidity and the sulphuric acid determined as usual.

With the vegetable materials the acidulated solution was evaporated to dryness and heated to dehydrate any silica which might have been present.

Nitric Acid Method.—Except that only 2 grams of the sample were taken, the method was carried out as described by Fraps.[3] The material was placed in a 4-inch porcelain evaporating dish, 20 cc. of concentrated nitric acid added and the mixture heated on the water-bath, cautiously at first and then at the temperature of boiling-water. When frothing had ceased and the solution was partly evaporated, 10 cc. of a 5 per cent. solution of potassium nitrate were added and the mixture evaporated to dryness and ignited, at first very cautiously over a Bunsen burner and finally

[1] This Journal, 24, 142.

[2] In one case it was necessary to filter at this point as the crucible had been attacked by the peroxide.

[3] This Journal, 24, 347.

over the blast-lamp until the residue was white. The residue was dissolved in hydrochloric acid, evaporated to dryness and heated for some time at 110° to 120° to render silica insoluble. Finally the residue was taken up with water and a little hydrochloric acid, filtered, the filtrate brought to the desired bulk and acidity and the sulphuric acid determined as usual.

With each method about 2 grams of the sample were used in each case and the final precipitation of barium sulphate was made in a solution of about 150 cc. containing about 2 cc. of concentrated hydrochloric acid. The amount of sulphur introduced by the reagents was determined for each method by making a "blank" test with sugar or benzoic acid.

Six samples were used in comparing the three methods. These were: (1) dried lean beef; (2) curd precipitated from cows' milk by acetic acid and reduced to a fine, dry, neutral powder; (3) coagulated yolk of egg, dried, ground and partially extracted with ether; (4) coagulated white of egg, dried and ground; (5) wheat bran; (6) dried beans, outer coating and germ removed before grinding. All of these samples were analyzed in the air-dried state. The results obtained are shown in the following table:

	Percentage of sulphur found.		
Substance.	Compressed oxygen method.	Hydroxide-peroxide method.	Nitric acid method.
Dried lean beef	0.815	0.811	0.679
Dried curd	0.610	0.608	0.495
Yolk of egg	0.822	0.819	0.810
White of egg	1.408	1.421	1.146
Wheat bran	0.264	0.259	0.182
Beans	0.217	0.229	0.165
Average	0.689	0.691	0.580

While the results by the first two methods are practically identical, those obtained by the nitric acid method are lower, the average amount of sulphur found being about five-sixths of that present. A part of this discrepancy is probably due to mechanical loss. Carrying out the method as described it was found in most cases that on heating the residue left on evaporation after the addition of the nitrate, no matter how slowly the heat was applied, there was a short period of vigorous oxidation at about the time the

material had become thoroughly charred. At this point there may easily have occurred a very slight mechanical loss of substance. It seems probable, however, that the greater part of the discrepancy was due to volatilization of sulphur in some form of combination not sufficiently oxidized to stand the heat generated at this point. Such a loss could doubtless be avoided by repeated evaporation with nitric acid or by the addition of alkali along with the nitrate but the method would then become practically that of Salkowski. It is possible also that by sufficient experimentation one might find the proportions of substance, acid, and nitrate which would give good results with a single evaporation, but the proportions would probably differ according to the material to be analyzed and in the writer's hands the method did not promise sufficient advantage to justify such a study. If all loss of sulphur could be avoided, it would become necessary to guard against an absorption of sulphur from the gas flame when the residue is heated over the blast-lamp.

While the results obtained by the first two methods are equally accurate, the combustion in oxygen has some distinct advantages. It requires much less attention, complete oxidation being instantaneously obtained with no danger of loss by volatilization. No reagents are used except the compressed oxygen and a little hydrochloric acid, both of which are apt to be free from sulphur, whereas it is difficult to obtain an alkali which does not contain an appreciable amount. Moreover, by doing away with the use of alkali any danger of absorption of sulphur compounds from the air of the laboratory is avoided and the solution in which the final precipitate is obtained is free from any large amount of foreign salts.

THE DETERMINATION OF PHOSPHORUS.

The following three methods for determination of phosphorus were compared.

Compressed Oxygen Method.—The combustion was carried out as described above. The ash in the platinum combustion capsule was dissolved by means of strong nitric acid and this solution added to the rinsings of the bomb and the whole boiled and then allowed to cool. Ammonia was then added in excess and the solution slightly acidulated with nitric acid and precipitated with molybdate

solution, the ammonium phosphomolybdate being afterward dissolved and the phosphoric acid precipitated with magnesia mixture in the usual manner. The details of manipulation recommended by the Association of Official Agricultural Chemists[1] were here followed, especial care being given to the conditions of the final precipitation.

Sodium Carbonate Method.—The sample was mixed in a platinum dish with 6 or 7 grams of dry sodium carbonate and 3 or 4 grams of the latter spread over the mixture. The dish was then heated carefully over a Bunsen burner until all danger of vigorous reaction was past. The heat was then raised and pulverized potassium nitrate added in small portions, the mass being occasionally stirred with a platinum rod. This was continued until the mass was entirely white, the whole amount of nitrate added being usually about 1 gram. After cooling, the fusion was transferred to a beaker, dissolved in water and nitric acid, and the determination completed as described above.

Sulphuric Acid and Ammonium Nitrate Method.—This was carried out essentially as described by Neumann.[2] The sample is placed in a Kjedahl digestion flask, 20 cc. of concentrated sulphuric acid and 10 grams of ammonium nitrate added, and the mixture heated carefully until frothing ceases, then allowed to cool somewhat and 10 grams more of ammonium nitrate added and the digestion continued until organic matter is entirely destroyed and a colorless solution obtained. This is allowed to cool, washed out into a beaker, about 15 grams of ammonium nitrate added, and the phosphoric acid determined by the molybdate-magnesia method as already described. This method had already been found to yield the same results as the carbonate method when applied to feces and urine, and the ease and rapidity of manipulation recommended it for trial upon substances containing a larger proportion of phosphorus in organic combination.

In comparing the three methods care was taken to secure approximate uniformity in the amounts of samples taken and of reagents used. Of the beef and of the beans about 2 grams were

[1] Bulletin 46, revised edition, Bureau of Chemistry, U. S. Dept. of Agriculture.

[2] Du Bois Reymond's Archiv., physiol. abth., (1897), pp. 552–553 through *Jahr. Thier chemie*, 27, 643.

taken for each determination; of each of the other samples about 1 gram was used.

The table below shows the results obtained by these three methods upon five of the samples already described (the white of egg being omitted as it contained only 0.1 per cent. of phosphorus, all of which remained in the ash), and on a sample of casein prepared in the laboratory and containing less than 0.5 per cent. of ash.[1]

	Percentage of phosphorus found.		
Substance.	Oxygen method.	Carbonate method.	Neumann's method.
Dried lean beef	0.490	0.492	0.499
Dried curd	1.341	1.335	1.327
Casein (air-dried)	0.789	0.789	0.797
Yolk of egg	1.364	1.368	1.366
Wheat bran	1.382	1.402	1.393
Beans	0.481	0.470	0.452
Average	0.975	0.976	0.972

The three methods thus yield practically the same results. As shown below it was found that most of the samples lost extremely little phosphorus when burned to ash in the usual manner. It is believed that these samples are fairly representative of ordinary food materials, rich in proteid matter. If so, the determination of phosphorus in food materials is attended with very much less danger of loss than the determination of sulphur.

In the case of the prepared casein about seven-eighths of the phosphorus was lost when the material was burned to ash, but in the determination of total phosphorus practically identical results were obtained by the three methods studied, indicating that these three methods are equally applicable to practically ash-free organic compounds of this nature as well as to food materials and ordinary physiological products.

LOSS OF SULPHUR AND PHOSPHORUS IN PREPARING ASH.

The proportion of sulphur which remains in the ash of animal and vegetable substances may not be of much significance in itself, yet as most ash analyses include the determination of sulphates and as the relation of total sulphur to sulphur in ash is being determined in some cases[2] it was thought advisable to include it here.

[1] For this sample the writer is indebted to Mr. P. B. Hawk, of the Department of Physiological Chemistry of this University.

[2] Fraps: This Journal, 23, 199; 24, 346.

In the case of phosphorus the loss in preparing the ash is in most cases much smaller and in view of the large number of recorded determinations of phosphorus in the ashes of animal and vegetable materials the relation of this to the total phosphorus becomes a matter of considerable importance.

The percentages of total ash in the air-dried samples, of total sulphur and phosphorus, and of sulphur and phosphorus which remained when the material was reduced to ash in the usual manner,[1] are shown in the following table:

SULPHUR AND PHOSPHORUS REMAINING IN ASH.

Substance.	Total ash. Per cent.	Percentage of sulphur.		Percentage of phosphorus.	
		Total.[2]	In ash.	Total.[3]	In ash.
Dried lean beef	2.21	0.813	0.036	0.494	0.457
Dried curd	8.10	0.609	0.072	1.334	1.332
Yolk of egg	4.92	0.821	0.013	1.366	1.307
White of egg	5.22	1.415	0.206	0.105[4]	0.105
Wheat bran	6.58	0.262	0.016	1.392	1.392
Beans	3.02	0.223	0.036	0.468	0.461

Thus while the loss of phosphorus was practically *nil* in four cases and very small in the other two, the loss of sulphur ranged from over four-fifths to practically all of that present.

It should be noted that the sample of curd contained, in addition of some of the salts originally present in the milk, a small amount of sodium acetate, formed by neutralization of the acetic acid used in precipitation, which doubtless aided in the retention of sulphur and phosphorus. As already stated, the sample of prepared casein used in the work on phosphorus lost about seven-eighths of its phosphorus on being burned to ash. In the case of the yolk of egg the reduction of the ash to whiteness required two or three hours at the moderate red heat which was used. When the burning was completed over a blast-lamp the ash was reduced to 4.19 per cent., and the phosphorus remaining in the ash to 1.143 per cent. of the original material.

CONCLUSIONS.

For the determination of sulphur the method of combustion in compressed oxygen is preferred. Equally good results were ob-

[1] Bulletin 46, revised edition, Bureau of Chemistry, U. S. Department of Agriculture.
[2] Averages of results by the oxygen and alkali methods.
[3] Averages of results by the three methods used.
[4] Determined by the carbonate method.

tained by the hydroxide-peroxide method but the manipulation is less convenient. The nitric acid method as used gave low results.

In the determination of phosphorus practically identical results were obtained whether the material was oxidized by combustion in oxygen, by heating with carbonate and nitrate, or by boiling with sulphuric acid and ammonium nitrate. For the analysis of food materials and physiological products the last-mentioned method will probably be found most convenient, especially in laboratories where the Kjeldahl method for nitrogen is largely used.

In analyzing animal and vegetable materials there is very much greater danger of loss by volatilization of sulphur than of phosphorus.

The writer desires to express his indebtedness to Prof. W. O. Atwater of Wesleyan University, who encouraged this work in many ways and in whose laboratory a large part of it was done, and to Mr. Emil Osterberg who assisted with many of the determinations.

NEW YORK CITY,
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FURTHER NOTES ON THE BROMINE ABSORPTION OF OILS.

BY PARKER C. MCILHINEY.

Received July 17, 1902.

IN TWO papers published in the Journal of this Society,[1] the writer submitted a method of examining fats and oils in which the substance to be examined was acted upon by bromine dissolved in carbon tetrachloride. The most important advantage claimed for the method was that if the oil or fat contains substances with which bromine reacts to form substitution products, the fact will be made known by the production of a certain amount of hydrobromic acid which is determined in one part of the process. The ordinary animal and vegetable oils and fats, such as olive oil, lard, cottonseed oil, linseed oil, etc., which are practically pure glycerides, absorb almost the whole of the bromine which disappears during its action upon them by direct addition, that is to say, the bromine unites with pairs of carbon atoms which had previously been connected by double or triple bonds, and consequently but

[1] Vol. 16, 275, and 21, 1084.

little hydrobromic acid is produced by the reaction. The analytical process gives, for each test made, two figures, one showing the bromine absorbed by direct addition and the other the amount which has substituted hydrogen.

The most frequent adulterants of fatty oils are petroleum and rosin, both of which are relatively cheap. Both of these react with bromine to produce hydrobromic acid, and thereby give very distinct indications of their presence in other oils. An extended application of the process has not resulted in any modifications except in one instance, when we have to deal with a substance which is partly organic and partly inorganic. This condition occurs in boiled linseed oil and more particularly in driers. The oxides of lead and of manganese which are natural constituents of these substances, and also the lime which is sometimes present, neutralize, as might be expected, a part or the whole of the hydrobromic acid, which may be formed by the reaction of bromine with such an adulterant as rosin or petroleum. Consequently when metallic compounds are present it is not safe to assume that an oil is free from rosin simply because its bromine substitution figure is low. If there is any considerable amount of rosin the small amount of lead and manganese present in boiled oil will not obscure the indications, especially as not only is the substitution figure of rosin very high (75 or thereabouts as compared with 3 for linseed oil), but its addition figure is very low, only about 5 as against 105 for linseed oil. On account of the small proportion of driers usually added, it may easily happen, however, that a sample of boiled oil which contains a drier partly composed of rosin or of mineral oil may give bromine figures which are not at all suspicious. If the oil is adulterated with rosin or with mineral oil in larger amounts, 5 per cent. or more, such as would naturally be added if the purpose was to cheapen the product, the lowering of the addition figure will be sufficiently marked to attract attention even if mineral bases are present in sufficiently large amounts to entirely neutralize the hydrobromic acid, and the occurrence of so much mineral base is not likely.

It may be remarked that the iodine figure of rosin is about 0.8 of that of linseed oil, and that the adulteration with rosin may be quite serious without any marked lowering of the Hübl figure.

In the case of the analysis of driers used in making boiled oil, the same remarks apply, but in a much greater degree.

To sum up the matter we may say that the introduction into an oil of mineral bases, such as lime and the oxides of lead and of manganese, decreases the bromine substitution figure given by the oil, and this reduction must be taken account of in the analysis of boiled linseed oil and of driers.

It may be of interest to give some account of the effect of varying conditions upon the results obtained by the process. First with regard to the time required for the contact. A number of experiments have been made to ascertain how long a time is required for the reaction to be completed. It appears, as a result of the experiments, that as far as the reaction of bromine and the pure glycerides is concerned, the reaction goes on to completion in a very short time, probably one minute or less, even in the case of oils absorbing most halogen, such as linseed oil. This appears to be true, generally, providing the absorption is entirely by addition. If part or all of the absorption of halogen is by substitution, the amount absorbed varies, as it is natural to expect that it would, with the time of contact between halogen and the substance. Lewkowitsch[1] takes exception to the author's conclusion that on account of the great variation in the results caused by differences in the time occupied by the experiments, the iodine figure of rosin is of little value as a "constant". He calls attention to the fact that the Hübl figure varies with the time of contact in the case of other substances than rosin. In reply it may be said that in the case of unsaturated glycerides the importance of the time factor is insignificant as compared with its importance when the halogen absorption is mostly by substitution. The writer still feels that the iodine figure of rosin is hardly definite enough to entitle it to recognition as a "constant".

A number of experiments were made to compare the rapidity with which bromine in carbon tetrachloride solution acts upon such a material as common rosin, with the rapidity of the action of Hübl's solution on the same material.

The bromine absorption of a sample of W. G. rosin was determined in four experiments, in one of which the reagent was allowed to act upon the rosin for two minutes, in another for

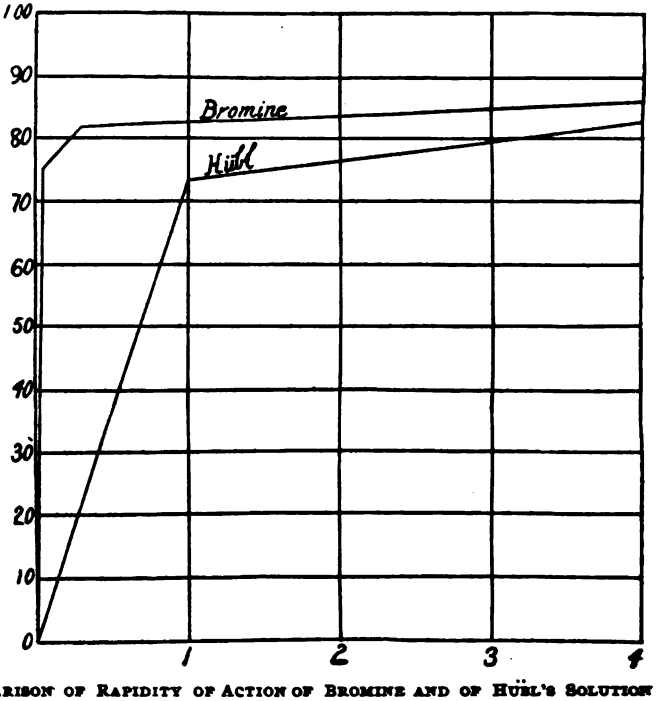
[1] "Oils, Fats, and Waxes," second edition, p. 235.

eighteen minutes, in a third for sixty-nine minutes, and in a fourth for twenty hours; the results were as follows:

Time.	Total bromine absorption. Per cent.
Two minutes	160.8
Eighteen minutes	174.5
Sixty-nine minutes	178.0
Twenty hours	213.4

Similar experiments with Hübl's solution of iodine were previously reported by the author.[1] The same sample of rosin was used in both sets of experiments. The results obtained were as follows:

Time.	Total iodine absorption. Per cent.
One hour	126.7
Two hours	133.1
Four hours	142.0
Eight hours	144.8
Eighteen hours	160.3
Fifty-two hours	172.6



COMPARISON OF RAPIDITY OF ACTION OF BROMINE AND OF HÜBL'S SOLUTION UPON ROSIN.

The two sets of experiments are compared graphically in the

[1] This Journal, 16, 56.

figure. The highest absorption found in each case is taken as 100, the lower absorptions being reduced to the same basis and represented in the figure as ordinates. The abscissas represent time in hours. It will readily be seen from the figure that the absorption of bromine is much more nearly complete at the end of a short experiment than that of iodine in the determination of the Hübl figure, and consequently that the bromine absorption of such a material as rosin is a much more definite figure and less affected by the length of the experiment than the Hübl figure is for the same substance, though by no means a "constant."

Rosin may be taken as one of the best examples of the absorption of halogen purely by substitution, the addition figure being very low indeed, though the total absorption is high.

A series of five experiments, made to determine the effect of varying excess of bromine, gave the following results; a sample of pure linseed oil was used for the experiments:

Percentage of excess of bromine.	Total bromine absorption. Per cent.
16.5	92.4
36.4	95.5
42.1	98.3
81.2	101.0
104.3	103.5

It will be seen that an excess of bromine amounting to 100 per cent. or more of that absorbed by the oil is necessary in order that the reaction may speedily go on to completion.

Another series of experiments was made to determine the effects of varying temperature and of the presence or absence of moisture in the oil. The bromine figure of a sample of linseed oil was determined in four ways:

First, in the ordinary way at the room temperature 20° C.

Second, with 10 cc. of water added to each test at the room temperature.

Third, with 10 cc. of water added to each test and the bottles kept immersed in melting ice.

Fourth, with 10 cc. of water added to each test and the bottles heated to 30° C.

The experiments were all carried on at the same time. The shortest test was eighty-eight minutes and the longest one hundred and eighty minutes.

The results obtained were as follows:

	Total bromine absorption.	Bromine addition.	Bromine substitution.
Dry, ordinary condition.....	110.2	104.8	2.7
10 cc. water, ordinary temperature..	108.6	104.0	2.3
10 cc. water, cooled.....	109.8	104.0	2.9
10 cc. water, heated.....	113.2	103.0	5.0

It is noteworthy that the results appear to be but slightly affected by the variations introduced and particularly that the presence of water seems to be without serious effect.

FIXATION OF PHOSPHORIC ACID IN THE SOIL.

By J. T. Crawley.

Received June 11, 1908.

It has been known for a long time that when soluble phosphates are applied to the soil, they become fixed by the bases, lime, iron, etc., and are not leached from the soil to any very considerable extent by rain or irrigation waters. By this process water-soluble phosphoric acid is "reverted" or changed to a combination not soluble in water. This is akin to the fixation of potash and ammonia, which are changed into insoluble combinations in the soil.

This is a wise provision of nature and prevents salts and bases in the soil which have been rendered soluble by weathering and other agencies from being washed out and lost from the soil; and it enables the agriculturalist to apply certain forms of soluble fertilizers to growing crops without fear of losing them in the drainage waters. But what becomes of the water-soluble phosphoric acid applied as a fertilizer; is it fixed near the surface, or is it well distributed throughout the soil where the roots of plants can get it?

The following investigation was undertaken for the purpose of determining to what extent water-soluble phosphoric acid is distributed through the soil before it becomes fixed. In certain sections of these islands the cane grows by irrigation; in other sections the rainfall is ample. Where irrigation is practiced the soluble fertilizer is scattered along the cane row, in some cases covered, in other cases not, and followed up within a day or two by irrigation. Three or four inches of water would represent an

average irrigation. Usually the water disappears in the soil within twenty or thirty minutes of application. Where rainfall is depended upon, fertilizers are covered up.

APPARATUS AND METHODS.

The most conclusive and determinate method would be to apply phosphoric acid in water solution to the soil, and then, by making analyses of the soil, find where it has been fixed. This, however, is not practical since our chemical methods are not sufficiently delicate to detect slight differences in the amount of this acid, and were a soil analyzed before and after the application of an ordinary dose of phosphoric acid, this amount would not be detected. The lysimeter method is the next best; a given weight of phosphoric acid is applied to the soil, followed by an excess of water, the drainage water caught and analyzed. The difference between the amount of acid applied and that found in the drainage is the amount abstracted and held by the soil. By varying the depth of soil in this experiment we find the depth at which the phosphoric acid is held. Boxes, 9 in. cube, were made, several holes bored in the bottom for the purpose of allowing the drainage water to escape, and varying depths of soil placed in them. Ten grams of double superphosphate were applied in each case, which is as large an amount as is applied in the cane rows to a space 9 inches by 9 inches. In each case 4800 cc. of water were added, this amount being probably an average irrigation. Notes were made of the time necessary for the water to percolate through the soil, and the total time of draining.

RESULTS.

I. Experiments with dark-colored soil from Makiki. This soil contains more phosphoric acid soluble in weak vegetable acid solutions than any other Hawaiian soil thus far examined.

(1) Six inches of soil; water began percolating through the bottom of the soil at end of six minutes, and 1790 cc. of water were recovered within one-half hour, when drainage was practically completed. The 1790 cc. of water contained 0.023 gram P_2O_5 or 0.57 per cent. of total applied.

(2) Six inches of soil; the phosphate was covered up in the moist soil and allowed to stand over night. Water began drain-

ing within two minutes, and 3300 cc. were drained in forty minutes, containing but a trace of phosphoric acid.

II. Typical red soil from the Honolulu plantation.

(1) Six inches of soil; water began draining in two minutes, and finished draining in forty minutes. Recovered 2072 cc. water containing 0.1113 gram P_2O_5 or 2.78 per cent. of total applied.

(2) Six inches of soil containing 20.72 per cent. moisture; phosphate covered up and allowed to stand over night; began draining in three minutes; finished draining in fifty minutes. 2320 cc. of water were recovered, containing 0.0134 gram P_2O_5 or 0.34 per cent. of total applied.

(3) Three inches of soil; began draining in one minute; finished draining in thirty minutes. Recovered 3130 cc. of water containing 0.35 gram P_2O_5 or 8.75 per cent. of total applied.

(4) Three inches moist soil; phosphate covered up and allowed to stand over night. 2886 cc. of water were recovered, containing 0.0408 gram P_2O_5 or 1.02 per cent. of total applied. The soil and phosphate were allowed to stand two days. Two liters of water were poured over it, of which 1700 cc., containing 0.0048 gram P_2O_5 or 12 per cent. of total applied, were recovered. After standing two days this was subjected to a further leaching, the drainage containing but a trace of phosphoric acid.

(5) One inch of soil; began draining in ten seconds; finished draining in nine minutes. Recovered 4260 cc. water containing 1.866 grams P_2O_5 or 46.65 per cent. of total applied.

(6) One inch of soil; phosphate covered up and allowed to stand four hours before irrigation. Drainage water contained 0.274 gram of P_2O_5 or 6.85 per cent. of total applied.

(7) One inch of soil; phosphate covered up and allowed to stand over night. Drainage contained 0.2928 gram P_2O_5 or 7.32 per cent. of total. Same after standing two days and washing with two liters of water, yield 0.033 gram P_2O_5 or 0.82 per cent of total.

Putting these results in tabulated form we have:

TABLE I.—SHOWING THE AMOUNT OF PHOSPHORIC ACID HELD BY THE SOIL.

Depth of soil. Inches.	Black soil, when irrigated.	P_2O_5 retained. Per cent.	Red soil, when irrigated.	P_2O_5 retained. Per cent.
6	Immediately	99.43		
6	After fifteen hours	100.00		
6			Immediately	97.22
6			After fifteen hours	99.66
3			Immediately	91.25
3			After fifteen hours	98.98
3			Same after two days	99.88
1			Immediately	53.35
1			After four hours	92.68
1			After fifteen hours	99.18
			Same after two days	

From this we see that when the application of the fertilizer is followed immediately by irrigation, (1) more than one-half the phosphoric acid remains in the first inch of soil, more than nine-tenths in three inches, and practically the whole within six inches of the surface; (2) when an interval of fifteen hours intervenes between the application and the irrigation, more than nine-tenths of the phosphoric acid is retained by the first inch of soil and practically the whole by the first three inches. These conclusions are rather startling, inasmuch as it has been heretofore believed that water-soluble phosphoric acid, when applied to the soil, becomes pretty well distributed throughout the first eighteen inches or two feet of the soil when it is easily accessible to the roots of the plants. This bears on the question of the relative value of water-soluble and so-called citrate-soluble or "available" phosphoric acid. At the various experiment stations in the United States the same or very nearly the same valuation is put upon the two forms. Where there is a difference it is rarely more than 1 cent. per pound in favor of the water-soluble. Certainly on Hawaiian soils where the phosphoric acid becomes reverted at the surface, or very near the surface, the two forms have very nearly the same value, for even under the most favorable circumstances the water-soluble phosphates are disseminated throughout the soil but sparingly. On the other hand, in cases where fertilizers are applied and covered up a few hours before irrigation practically all of the phosphoric acid becomes reverted and remains near the surface. Also on plantations depending on rainfall where the fertilizers are applied and covered up, water-soluble and reverted

phosphoric acid have practically the same value, as the water-soluble becomes reverted and subsequent rains cannot wash it down to the roots of the plants, nor disseminate it throughout the soil. This is a possible explanation of a fact which I have set forth in former papers; namely, that phosphates have not shown as good results on Hawaiian soils as the other fertilizer ingredients —nitrogen and potash. It takes considerable cultivation to disseminate the phosphates throughout the soil, and although they may be deficient, yet an application is not followed by the immediate results that the planter expects.

Seeing that the water-soluble phosphoric acid is taken up so readily, a further experiment was made to determine the *total capacity* of the soil to fix phosphoric acid. 800 grams of red soil and 50 grams of double superphosphate containing 20.58 grams water-soluble phosphoric acid were thoroughly mixed together. This mixture was kept moist to promote the chemical action, and samples were withdrawn from time to time to estimate the water-soluble acid.

March 26th, 800 grams soil and 50 grams double superphosphate mixed; March 27th, 41.6 per cent. of P_2O_5 had become fixed; March 29th, 57.7 per cent. of P_2O_5 had become fixed; April 3rd, 73.0 per cent. of P_2O_5 had become fixed; April 17th, 85.65 per cent. of P_2O_5 had become fixed.

Or, taking 3,500,000 pounds as the weight of one acre of soil to the depth of 1 foot, we find that this soil absorbed:

After one day 35,235 pounds P_2O_5 per acre to depth of 1 foot; after three days 48,872 pounds P_2O_5 per acre to depth of 1 foot; after eight days 61,431 pounds P_2O_5 per acre to depth of 1 foot; after twenty-two days 72,545 pounds P_2O_5 per acre to depth of 1 foot.

This latter figure would represent all the phosphoric acid in 181 tons of acid phosphate.

These astonishing figures lead to a consideration of the nature of the soils experimented with, and the reason for the rapid and great fixation of phosphoric acid by Hawaiian soils. On p. 99, *et seq.*, of Maxwell's "Lavas and Soils of the Hawaiian Islands" will be found a comparison of Hawaiian and American soils, in which it is shown that Hawaiian soils are very much more basic than American soils.

TABLE II.

Soils.	Basic constituents. Per cent.	Acid constituents. Per cent.
Hawaiian	63.717	36.458
American	18.980	81.014

Whereas the American soils from which these figures were drawn contain but 13.250 per cent. iron and aluminum oxides, the Hawaiian soils contain 59.24 per cent.

All Hawaiian soils are very basic, and these bases are probably in a condition to seize at once the phosphoric acid and hold it. The American soils being much older than Hawaiian soils the soluble bases have been washed out, the soils are less basic in character, and will probably hold very much less phosphoric acid than the Hawaiian soils. Following is an average of a number of analyses of dark red soils, and the soil from the Honolulu plantation would not differ very materially from these figures.

TABLE III.—DARK RED SOILS.

	Per cent.
Insoluble matter	37.20
Moisture	6.16
Combustible matter	11.33
TiO_2	2.59
P_2O_5	0.19
SO_3	0.31
CO_2	0.18
CaO	0.34
MgO	0.44
Fe_2O_3	22.94
Al_2O_3	16.84
Mn_3O_4	0.42
K_2O	0.39
Na_2O	0.75
	100.08

With soils of this general composition it would be strange if their absorptive power of phosphoric acid were not great.

HONOLULU, H. I.

THE ESTIMATION OF SOIL ACIDITY AND THE LIME REQUIREMENTS OF SOILS.

By F. P. Veitch.

Received August 15, 1900.

Within the past few years, it has been definitely shown that the reaction of a soil exerts a marked influence on its crop-producing power. While the reaction affects the chemical and the physical condition of the soil to a considerable extent, the growth of plants is more directly affected by the action of the acids on the plant roots, and upon the micro-organisms of the soil.

The importance of the matter has led to the elaboration of several methods for determining the amount of acids in soil, but, owing to the exceedingly small amount usually present in ordinary arable soils, the influence of other material, and the constant changes taking place in the soil, none of these methods has shown a close relation between crop production and the amount of acidity as determined by any of the methods. Wheeler, Hartwell, and Sargent[1] have recently made a critical examination of the methods which have been proposed for this purpose, checking the chemical methods by field experiments. The investigators were unable to correlate the chemical results obtained by any of the methods examined with the field results, but regarded as promising the titration of dilute ammonia which had been in contact with the soil for some time, and also a method based on the evolution and estimation of the carbon dioxide freed from calcium carbonate by the acid soil on boiling them together in water.

It has not seemed advisable to the writer to give more study to either of these methods, because any solution placed in contact with a soil, no matter whether acid or alkaline, will be decreased in strength through adsorption or physical reaction between the solution and the soil; and we have no certain means of measuring the amount thus adsorbed. Further, owing to the deflocculating power of ammonia, it is practically impossible to get even an approximately clear filtrate or supernatant liquid, and the amount of acid as determined is more or less affected by this fact. With regard to the evolution and estimation of carbon dioxide, the

[1] This Journal, 22, 153.

evolution continues indefinitely, and whether it is due to reaction between the soil and the carbonate or to the oxidation of the organic matter of the soil is not definitely known, though it is probable that it is more largely due to the first-mentioned reaction.

After a great deal of experimenting the writer has devised a method in which lime-water is used to neutralize the acid material in the soil. The method is based on the fact that the small excess of lime-water present, after the neutralization of the acid material, is converted into carbonates and bicarbonates, the boiling solution of which gives an alkaline reaction with phenolphthaleïn.

No effort has been made to secure great refinement or close duplication of results, because the problem is a practical one in which the application of several hundred pounds of lime, more or less, per acre has but little economic or agricultural significance. It may be said, however, that the writer has reason to believe that the method will give duplicate results accurate to one hundred pounds of lime per acre foot of 3,500,000 pounds. The method is as follows:

For the preliminary test, to three portions of 10 grams each of the soil in platinum dishes add 50 to 60 cc. of distilled water, and different amounts of standard lime-water. For example, to the first 10 cc., to the second 20 cc., and to the third 30 cc. of lime-water are added. Dry down at once on the steam-bath, transfer to a stoppered Jena flask with 100 cc. of distilled water, allow to stand over night, with occasional shaking, filter (the filtrate should be clear or but faintly turbid), take 50 cc. in a Jena beaker, add a few drops of phenolphthalein solution, and boil until the appearance of the pink color, or in the case where no color is developed to a volume of about 5 cc. Then with the two portions of treated soil, one of which has been rendered alkaline by the added lime-water and the other of which is still acid, as guides, prepare three fresh portions of 10 grams each, and add lime-water as before, except that the amount added to a dish differs from that added to another, by only one or two cc. Dry, allow to stand, filter, and treat exactly as before; the smallest amount of lime-water which gives the characteristic pink with phenolphthaleïn is taken as the acidity equivalent of the soil. From the data thus obtained, the acidity and lime requirements of the soil may be calculated.

The results which have been obtained with this method are given in Table I. The amount of lime (CaO) required to neutralize the acids in an acre foot of 3,500,000 pounds is also included. 1 cc. of calcium hydroxide to 10 grams of soil is approximately 450 pounds of lime per acre.

TABLE I.

		50 cc. filtrate boiled.		Lime (CaO) required per acre foot of 3,500,000 pounds.
		Acid with cc. $Ca(OH)_2$.	Alkaline with cc. $Ca(OH)_2$.	
No. 1	Summit, R. I	20	25	11,250
No. 2	Jamestown, R. I	..	8	3,600
No. 3	Harrisville, R. I	10	15	6,750
No. 4	Foster Center, R. I	25	32	14,300
No. 5	Niantic, R. I	6	8	3,600
No. 6	South Portsmouth, R. I	30	35	15,750
No. 7	Hamilton, R. I	17	18	8,100
No. 8	Slocumville, R. I	54	56	25,200
C	Coarse sand used in greenhouse	3	4	1,800
No. 1	A. O. A. C. sample 1900	9	10 10	4,500
No. 3	A. O. A. C. sample 1900	50	52 52	22,500
No. 4	A. O. A. C. sample 1900	..	1	450
No. 3	A. O. A. C. sample 1901	8	9	4,050
No. 4	A. O. A. C. sample 1901	1	2	900
No. 5	A. O. A. C. sample 1901	1	2	900
5118	Leonardtown loam, Md	4	5 5	2,250
5127	Leonardtown loam, Md	8	10	4,500
5112	Norfolk loam, Md	4	5	2,250
5131	Norfolk sand, Md	0	1	450
4244	Conowingo Barrens, Md	4	5	2,250
3624	Fine sandy soil, Fla. (much organic matter)	7	8	3,600
A	Gabbro soil, Md	10	12 12	5,400
O	Lime Expt. plot, Md. Station, 60 bushels per acre	1	2	900
B	Lime Expt. plot, Md. Station, no lime	5	6 6	3,150
D	Md. phosphoric acid plots	1	2 2	900

The samples from Rhode Island Nos. 1 to 8 are samples kindly furnished by Dr. Wheeler, and are the same upon which he worked in the investigation previously referred to. Owing to the

scarcity of material, closer readings than those given in the table could not be made, on these samples; but the readings made on other samples show that much closer readings could probably have been made here.

A summary of Wheeler's results on these soils, field and laboratory, is given in Table II. To this has been added the results obtained by the lime-water method on these same samples by the writer. For a more satisfactory comparison, the lime-water results have been calculated to their nitrogen equivalents, and the acidity of the samples as expressed in pounds of lime (CaO) per acre foot of 3,500,000 pounds has been included.

These results, while somewhat unsatisfactory, are not so surprising when we consider the different soils and the number of factors involved in plant production which are influenced and modified by the addition of lime to a soil, even though that soil may be liberally supplied with available plant food. It is of interest to note that soils Nos. 6, 8 and 9 produced such large crops of beets after liming, although the soils still remained very acid. In other words, after liming, beets were not as sensitive apparently to an acidity equivalent to 20,000 pounds of lime per acre as they were to half this amount on unlimed, but different soils, a fact which possibly indicates that the toxic effect of acids is not so great in the presence of large quantities of soluble lime-salts.[1] This fact is highly important practically and may explain why small applications of lime are often as beneficial as large. It may also explain why slightly acid soil will often produce certain crops, clover, for instance, which will not grow on other soils which are even less acid.

It is also interesting to note that the relative acidity of these soils is the same, whether determined by treatment with ammonia, as was done by Wheeler, or by treatment with lime-water, as was done in this laboratory.

Perhaps the most striking point brought out in the table is the apparent relation of alkali neutralized by the soil to the total humus of the soil. While this relation does not seem to be exceedingly close, it is clearly apparent and is very suggestive in lending support to the hypothesis that the acidity of soil is gener-

[1] *Vide* Ninth Annual Report R. I. Expt. Station p. 309; also Report 71, Bureau of Soils, U. S. Dept. of Agriculture.

TABLE II.—COMPARISON OF THE AMMONIA WATER, AND THE LIME-WATER METHODS.

Summarized from Wheeler's results.

	Yield of beets unlimed. Pounds per 1/20 acre.	Yield of beets limed. Pounds per 1/20 acre.	Increase due to liming. Pounds.	Total humus. Per cent.	Mgs. N in NH_3 retained by 10 grams soil.	Mgs. CaO retained by 10 grams soil lime-water method.	Mgs. N equivalent to CaO retained by 10 grams soil.	CaO required per acre foot to render the soil neutral. Pounds.	CaO still required per acre foot to render soil neutral after Wheeler's liming. Pounds.
No. 1 Summit, R. I.	47.4	92.9	45.5	1.73	19.6	32.0	16.0	11,250	6,250[1]
No. 2 Jamestown, R. I.	75.8	152.7	76.9	0.85	10.4	10.2	5.1	3,600	
No. 3 Harrisville, R. I.	151.5	207.3	55.8	1.46	14.1	19.2	9.6	6,750	1,750
No. 4 Foster Center, R. I	36.3	143.4	107.1	2.21	25.5	40.9	20.4	14,300	9,300
No. 5 Niantic, R. I	9.9	43.4	33.5	0.95	7.9	10.2	5.1	3,600	
No. 6 South Portsmouth	26.0	153.0	127.0	2.63	27.2	44.8	22.4	15,750	10,750
No. 7 Hamilton, R. I	14.5	131.8	117.3	1.60	15.8	23.0	11.5	8,100	3,100
No. 8 Slocumville, R. I	1.0	101.8	100.8	5.08	43.8	71.5	35.75	25,200	20,200
No. 9 Kingston, R. I.	6.6	161.4	154.8	5.15	36.1	66.6	33.3	23,400	18,400

[1] The figures in this column were obtained by subtracting the pounds of lime (CaO) applied to duplicate plots by Wheeler, from the figures given in the preceding column.

ally due to organic acids. In studying these figures, the fact should be borne in mind that neither the methods of determining acidity nor total humus are very exact, and there may be errors in these various determinations, which, if eliminated, would make the relation pointed out much more striking.

As with all other chemical methods used in soil work, the method must not only give accurate results, but these results must have an agricultural significance. Let us see how well the proposed method satisfies the conditions.

The development of the pink color with phenolphthalein in the boiled aqueous extract of a soil is doubtless only a question of the volume of extract which is boiled down; even very acid soils will, on long-continued treatment with much water, yield an extract which, on concentration, will give an alkaline reaction with this indicator. A great number of determinations made in this laboratory shows that a soil which gives an alkaline reaction with litmus paper also gives an aqueous extract which is alkaline to phenolphthalein when treated with water in the proportion of 1:10, and 50 cc. of the extract is boiled. Numerous determinations of the reaction of soils from all over the country indicate very strongly that those soils which are alkaline to litmus and to phenolphthalein under the conditions above described are always more productive soils than contiguous soils which are acid to these indicators. These are the reasons why the proportion of soil to water, and the amount of filtrate to be boiled, as given above, were adopted.

As has been said, we have no method by which we can determine how much of the lime taken up by the soil is actually neutralized by the acid material of the soil, and how much is simply adsorbed and held physically by the soil in such a manner that it does not pass into solution. This is the chief difficulty inherent in any titration method for determining soil acidity. Plus errors are thus introduced, and the acidity of a soil appears greater than it actually is. Experiments, in which soils of different nature were treated with known amounts of dilute ammonia (N/20), soda (N/50), and lime-water (N/20), and aliquot portions of the filtrate titrated both directly with acid, and also by adding an excess of acid and titrating back, showed in every instance that the amount of adsorbed alkali was greater than by the lime-water method. The figures in Table II show the same thing.

Theoretically, there is every reason to believe that adsorption is less under the conditions obtained in the lime-water method than in the titration methods, for, as we know, adsorption is actually greater from the more concentrated solution, and in the titration methods we must always expect to have more alkali present than is sufficient to neutralize the acid material of the soil, and to satisfy the soil's adsorptive power in the presence of such excess of alkali.

In the method above outlined, the amount of alkali which must be present is enough to neutralize the acid material plus a little more than the soil is able to hold against the solvent power of partially carbonated water. That this is so seems quite clear, and is strongly supported by the results in Table II, from which we see that in every case the lime equivalent to nitrogen retained by the soil is much less by the lime-water than by the ammonia-water method. The differences are much too large and regular to be accounted for either by errors or by differences due to neutralization of the acid material of the soil. Another point: It is more than likely that considerable reaction takes place between the non-acid material of the soil and ammonia, even in the cold. If there is any reaction between the lime-water and the material, it is reasonable to think that it is much less, because the very small excess of lime-water is immediately converted into carbonate and bicarbonate, as shown by the behavior toward phenolphthalein. Nevertheless we must regard all these methods as likely to give high results, owing to the probable combination of the alkalies with some silica and silica compounds, both reactions introducing plus errors. The smallest difference between the two methods occurs on No. 5, which is visibly a coarse sandy soil, and upon which adsorption would be expected to be at a minimum.

Reference has been made to the fact that Wheeler regarded as particularly promising a method based on the evolution of carbon dioxide from a mixture of soil and calcium carbonate in boiling water. He found that after boiling such a mixture (40 grams of soil and 4 grams of calcium carbonate) until apparently the evolution had become constant and hence the evolution of carbon dioxide set free by the acid material in the soil had ceased, that two more boilings of the same mixture yielded 0.016

and 0.048 gram of carbon dioxide. These results indicate the decomposition of calcium carbonate equal to 20.8 and 16.6 mg. of lime to 40 grams of soil. These figures are equal to 4.4 and 3.4 cc. of lime-water to 10 grams of soil. From this it would appear that the possible errors would be greater by this method than by the lime-water method.

As has been pointed out, in all these methods the possible combination of the lime with silica and other inorganic soil constituents, without the release of an equivalent of some other base, is a source of error which increases the actual acidity of the soil. Any difference in the methods in this particular would probably be in favor of the lime-water method. As a matter of fact, the adsorption of the added alkali appears to introduce no error greater than the working limits of the method, a fact which was shown by determining the acidity of two soils in natural condition, and also after they had been powdered. On the other hand, adsorption phenomena certainly vitiates the results by those methods based on the titration of an aqueous extract of the soil or of an alkali which has been in contact with the soil. Nor does it seem probable that the water-insoluble material of an acid nature produces an appreciable error in the method, there being every reason to suppose that these materials will be neutralized by the lime. Further, it is believed that under the conditions of the method, the results are not complicated by the reaction of free carbonic acid or by bicarbonates.[1] Viewed in any light, this method or any method based on the use of lime-water or lime carbonate as the neutralizing agent, must appear to one as being along the right line, imitating as it does actual field conditions.

Analytically considered, the method appears to be sufficiently reliable for practical purposes, and appears to be the best now available for the end in view.

Agriculturally considered, we have no positive direct data showing that the acidity of a soil as determined by analytical methods has a definite ratio to the crop production of that soil. The fact that those soils which are universally regarded as fertile, have an alkaline reaction to litmus paper and to phenolphthalein, when their aqueous extracts are boiled, as in the previously de-

[1] The data upon which this view is based will be given in full in a publication soon to appear from the Bureau of Soils, U. S. Dept. of Agriculture.

scribed method, furnishes strong evidence as to the agricultural significance of the results thus obtained, but so far no one has been able to show a close agreement between crop yields and the lime requirements of soil as determined by laboratory methods.

BUREAU OF SOILS, DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

THE ANALYSIS OF VANILLA EXTRACT.

BY A. L. WINTON AND M. SILVERMAN.

Received August 11, 1902.

HESS AND PRESCOTT, in papers published in this Journal,[1] have discussed the adulteration of vanilla extract and have described methods devised by them for the separation and determination of vanillin and coumarin, for the distinction of genuine from artificial extracts, and for the detection of artificial coloring-matter, all of which methods, with slight changes, are included among the "Provisional Methods for the Analysis of Foods", adopted by the Association of Official Agricultural Chemists.[2]

Preliminary to the examination of commercial extracts, under the Connecticut pure food law, we have subjected these methods to a critical investigation, the results of which, while substantiating in the main the accuracy of the methods, suggested certain modifications. The Hess and Prescott method for determination of vanillin and coumarin was found to be thoroughly reliable but susceptible of abridgment without diminishing its accuracy.

The methods as finally amended were employed in the analysis of five extracts made in the laboratory and sixty-two commercial extracts.[3]

METHODS OF ANALYSIS.

Determination of Vanillin and Coumarin. Modified Hess and Prescott Method.—The modified method differs from the original method in three details:

First. Two per cent. instead of 10 per cent. ammonia is used, and consequently a less concentrated ammonium chloride solution is obtained after neutralizing with hydrochloric acid, thus reducing the chance of carrying this salt into the extract.

[1] Vol. 21, 256, 721.

[2] Bulletin 65, U. S. Dept. Agr., Bureau of Chem., pp. 69–71.

[3] Conn. Agr. Expt. Sta. Rep. 1901, pp. 152–162.

Second. A greater bulk of ammonia is used, to diminish the error due to possible mechanical loss during shaking.

Third. The vanillin and coumarin are weighed after evaporation of the ether solutions, whereas in the original process they are not weighed until they have been redissolved in petroleum ether and again evaporated. This procedure not only materially shortens the process, but avoids the errors due to crawling of the solutions while redissolving and reevaporating. Any matter insoluble in the petroleum solvent is afterwards weighed with the dish and a correction introduced, but if care is exercised in the separation, this residue is insignificant. The evaporation of the petroleum extract is, however, necessary if melting-points are to be determined, but this evaporation can go on at leisure after obtaining the quantitative results.

A full description of the method follows:

Dealcoholize 25 grams of the extract in an evaporating dish upon a water-bath, at a temperature of about 80° C., adding water from time to time to retain the original volume. After removal of the alcohol, add normal lead acetate solution, drop by drop, until no more precipitate forms. Stir with a glass rod to facilitate flocculation of the precipitate, filter through a moistened filter, and wash three times with a few cubic centimeters of hot water. Cool the filtrate and extract with ether by shaking out in a separatory funnel. Use 15 to 20 cc. of ether at each separation, repeating the process three or four times, or until a few drops of the ether, evaporated upon a watch-glass, leave no residue. Place the combined ether extracts containing all of the vanillin and coumarin in a clean separatory funnel, and shake out four or five times with 2 per cent. ammonia, using 10 cc. for the first shaking, and 5 cc. for each subsequent shaking.

Set aside the combined ammoniacal solutions for the determination of vanillin.

Wash the ether solution into a weighed dish, and allow the ether to evaporate at the room temperature. Dry in a desiccator and weigh. Usually the dried residue is pure coumarin. Treat the residue with 5 to 10 cc. of cold petroleum ether, boiling between 30° and 40° C. and decant off the clear liquid into a beaker. Repeat the extraction with petroleum ether until a drop, evaporated

on a watch-glass, leaves no residue. Dry the dish for a few moments in a water-oven, cool and weigh. Subtract the weight of the dish and the residue (if any) from the weight previously obtained after evaporation with ether, thus obtaining the weight of pure coumarin. Allow the petroleum ether to evaporate at the room temperature, and dry, if necessary, in a desiccator. The residue should be crystalline and have a melting-point of 67° C. This, with the characteristic odor of coumarin, is sufficient for its identification.

Slightly acidulate the ammoniacal solution reserved for vanillin with 10 per cent. hydrochloric acid. Cool and shake out in a separatory funnel with four portions of ether as described for ether extraction. Evaporate the ether at room temperature in a weighed platinum dish, dry over sulphuric acid, and weigh. Treat the residue with boiling ligroin (boiling-point, 80° to 85° C.), decanting into a dry beaker. Repeat the treatment until all vanillin is removed. Dry the dish with residue (if any) for a few moments at 100° C. and weigh. Subtract the weight from the weight previously obtained after evaporating the ether. The difference is the weight of vanillin. Evaporate the ligroin at room temperature and dry in a desiccator. The residue should be crystalline, have a melting-point of 80° to 81° C. and have the characteristic odor and crystalline form of vanillin.

Hess and Prescott,[1] as a test of their process, determined vanillin and coumarin in two 25-gram portions of vanilla extract U. S. P., to each of which had been added 0.5 gram of pure coumarin. The following are their results: Vanillin (I), 0.3081 gram; (II), 0.2997 gram.[2] Coumarin (I), 0.4910 gram; (II), 0.4820 gram. These figures illustrate the accuracy of the process for determination of coumarin, but throw no light on its value for determination of vanillin, as the amount present was unknown.

As a further test of the Hess and Prescott method, we have made determinations in 25-gram portions of a solution containing the same amount of sugar and alcohol as vanilla extract U. S. P., to which weighed quantities of pure vanillin and coumarin had been added, proceeding as follows:

[1] This Journal, 21, 256.

[2] Owing probably to a typographical error, these amounts are about ten times what are usually present.

Method *A*. The original Hess and Prescott method, using ether in all extractions and 10 per cent. ammonia for separation of vanillin and coumarin.

Method *B*. Same as *A*, except that chloroform was substituted in all cases for ether.

Method *C*. Same as *A*, except that chloroform was used in the extraction of vanillin from the ammonia extract.

Method *D*. The modified method used by us, as already described.

In each case the separated vanillin and coumarin was weighed after the evaporation of the ether or chloroform (first evaporation), and only in a few instances was it reweighed after dissolving in the petroleum solvent and reevaporating (second evaporation). The results follow:

RESULTS OBTAINED BY VARIOUS MODIFICATIONS OF HESS AND PRESCOTT'S METHOD, ON MIXTURES CONTAINING KNOWN QUANTITIES OF VANILLIN AND COUMARIN.

	Vanillin.			Coumarin.		
Method.	Taken. Gram.	Found after first evaporation. Gram.	Found after second evaporation. Grain.	Taken. Gram.	Found after first evaporation. Gram.	Found after second evaporation. Gram.
A	0.0120	0.0101	0.0100	0.0170	0.0162	0.0165
B	0.0695	0.0723	0.0705	0.0975	0.0902	0.0900
C	0.0495	0.0490				
C	0.0280	0.0261				
C	0.0610	0.0630	0.0575	0.0855	0.0751	0.0740
C	0.0120	0.0136	0.0120	0.0170	0.0160	0.0162
C	0.0290	0.0280				
C	0.0495	0.0455				
D	0.0625	0.0636	0.0610	0.0875	0.0800	0.0786
D	0.0625	0.0620		0.0875	0.0796	
D	0.0625	0.0621	0.0585	0.0875	0.0803	0.0795
D	0.0625	0.0602		0.0125	0.0125	
D	0.0625	0.0630		0.0125	0.0124	
D	0.0625	0.0615		0.0125	0.0122	

From these figures it is evident that the process, both as originally described and as abbreviated by us, gives remarkably accurate results for vanillin and sufficiently accurate results for coumarin.

Where the amount of coumarin was large, there was an unac-

countable deficiency of this substance, but for the amounts present in extracts, which, in our experience, has not exceeded 0.0600 gram per 25 grams of extract, the method is all that could be desired. The melting-points of the coumarin and vanillin in all cases were close to the theory.

Without doubt, this excellent method is in all points the best that has yet been devised.

Tests for Caramel, Coal-tar Dyes, etc.—Valuable indications of the nature of an extract are obtained in the process of determination of vanillin and coumarin. Pure extracts of vanilla beans give, with lead acetate, a bulky, more or less glutinous, brown-gray precipitate, and a yellow or straw-colored filtrate, whereas purely artificial extracts colored with caramel give a slight, dark brown precipitate and a dark brown filtrate. If both vanilla bean extract and caramel are present, the precipitate is more or less bulky and dark-colored, and the filtrate is more or less brown. The solution remaining after extraction of the vanillin and coumarin with ether, if dark-colored, should be tested both for caramel and coal-tar colors.

In our experience the most satisfactory test for caramel is to shake with fullers' earth as recommended by Crampton and Simons.[1] If the color is due to caramel and a grade of fullers' earth is used, which experience has proved suitable, the solution, after filtering, is yellow or colorless. This test does not positively identify the color, as some other brown substances may give similar reactions, but no such substance is liable to be present in vanilla extract.

Amthor's test[2] for caramel has not given in our hands decisive results, and Hess' test,[3] owing to the formation of caramel from the sugar of the extract during the heating with acid, has given reactions in extracts known to contain none whatever of this substance.

Coal-tar dyes may be tested for by Arata's method.[4]

Determination of Total Residue.—Introduce into a flat-bottomed aluminum dish 10 grams of ignited sand and a short stirring-rod,

[1] This Journal, 21, 355; 22, 810.
[2] *Ztschr. anal. Chem.*, 24, 30.
[3] This Journal, 21, 721.
[4] *Ibid.*, 22, 582.

and weigh. Add 5 grams of extract and heat on a boiling water-bath, with constant stirring, until the bulk of the water is removed. Dry in a water-oven until the loss sustained in one hour is less than 2 mg.

The "total residue" not only includes the total solids, but also glycerin which is often present in such amount that the residue appears moist after drying. Owing to the slow evaporation of this substance, absolutely constant weight can not be secured but the loss is so gradual that the above method is usually sufficiently accurate.

Determination of Alcohol.—Dilute 25 grams to 150 cc. and distil into a 100 cc. pycnometer. Determine the specific gravity of the distillate at 15.5° C. and calculate the percentage by weight.

Determination of Cane-Sugar. Detection of Glucose.—Dissolve 13.024 grams (one-half the normal weight) of the material in about 80 cc. of water. Add 3 cc. of basic lead acetate and 2 cc. of alumina cream, make the volume up to 100 cc. and filter through a dry filter. Determine the rotatory power of the solution in a 200 mm. tube. To 50 cc. of the filtrate referred to above, add 5 cc. concentrated chemically pure hydrochloric acid. After thorough mixing, place in a cold water-bath and heat quickly to 68° C. After standing at that temperature for ten minutes, cool quickly, filter from lead chloride, if necessary, and examine in a 220 mm. tube, first at the room temperature and finally at 86° C.

Estimate the percentage of cane-sugar by Clerget's formula. A considerable plus reading at 86° shows the presence of glucose.

Determination of Glycerin.—Determine in 5 grams of the extract as directed for sweet wines.[1]

ANALYSES OF GENUINE AND ARTIFICIAL VANILLA EXTRACTS.

Five extracts were made in the Station laboratory, from different grades of beans, after the U. S. P. formula.

An extract of tonka beans was also prepared in the laboratory in the same manner as the vanilla extracts, substituting, however, tonka beans for vanilla beans.

Analyses of these extracts and of fourteen representative commercial extracts, both pure and adulterated, are given in the table:

[1] Borgmann: Anleitung zur Chem. Analyse des Weines, 2 Auf., p. 50. U. S. Dept. of Agr. Div. of Chem., Bull. 46, Revised ed., p. 63.

Analysis of Vanilla Extracts.

Serial No.		Vanillin.	Coumarin.	Total residue.[1]	Cane-sugar.	Glycerin.	Solids other than cane-sugar.	Alcohol by weight.	Coloring.
4562	U. S. P. Mexican beans	0.13	0.00	22.60	19.90	0.00	2.70	37.96	natural
4561	U. S. P. Mexican beans (cut)	0.07	0.00	23.10	19.20	0.00	3.90	39.92	"
4504	U. S. P. South American beans	0.22	0.00	22.00	19.00	0.00	3.00	38.58	"
4505	U. S. P. Bourbon beans	0.14	0.00	23.13	20.40	0.00	2.73	38.32	"
4506	U. S. P. Tahiti beans	0.11	0.00	21.75	20.00	0.00	1.75	38.84	"
4509	U. S. P. Tonka beans	0.00	0.21			...	...		"
4193	Commercial extract (not found adult'd)	0.08	0.00	21.84	10.36	8.87	2.61	40.00	"
4132	Commercial extract (not found adult'd)	0.18	0.00	13.52	0.90	10.76	1.86	27.51	"
4137	Commercial extract (not found adult'd)	0.15	0.00	16.43[2]	4 54	4.54	7.35[2]	21.27	"
4180	Commercial extract (not found adult'd)	0.09	0.00	16.72	15.44	0.00	1.28	20.90	"
4052	Commercial extract (not found adult'd)	0.22	0.00	22.66	20.00	0.00	2.66	23.79	"
4129	Adulterated commercial extract	0.22	0.08	0.86	0.47	0.00	0.39	6.34	artificial
4152	Adulterated commercial extract	0.68	0.15	14.00	10.64	2.42	0.94	17.32	natural
4179	Adulterated commercial extract	0.02	0.10	14.34[3]	0.75	0.00	13.59[3]	14.15	"
4141	Adulterated commercial extract	0.15	0.04	15.15	12.28	0.00	2.87	5.28	artificial
4078	Adulterated commercial extract	0.14	9.05	12.94	0.60	9.74	2.60	41.42	natural
4053	Adulterated commercial extract	0.24	0.18	14.62	10.92	0.00	3.70	11.91	"
4056	Adulterated commercial extract	0.07	0.00	14.35	11.20	0.00	3.15	31.72	artificial
3959	Adulterated commercial extract	0.06	0.23	36.16[2]	12.96	0.00	23.20[2]	7.53	"
3972	Adulterated commercial extract	0.01	0.09	13.44	11.14	0.00	2.30	9.68	"
3725	Adulterated commercial extract	0.44	0.11	26.54	21.00	0.00	5.54	10.73	"
4042	Adulterated commercial extract	0.06	0.05	35.50	31.88	0.00	3.62	13.36	natural

[1] Includes glycerin. [2] Contains glucose. [3] Contains invert sugar.

From the analyses of the U. S. P. samples it is evident that the percentage of vanillin bears no relation to the value of the extract. Sample No. 4562, made from Mexican beans costing $11.00 per pound, contained less than Nos. 4504 and 4505 made respectively from South American and Bourbon beans costing less than $7.00 per pound and but little more than No. 4506 made from Tahiti beans costing but $1.50 per pound. The average percentage of alcohol was 38.72 and of cane-sugar, 19.70. The residue other than cane-sugar ranged from 1.75 to 3.90 per cent. None of these extracts contained the slightest trace of coumarin; on the other hand, the Tonka bean extract contained 0.21 per cent. of coumarin but no vanillin.

The commercial extracts classed as "not found adulterated" appeared to have been made from vanilla beans, without addition of other coloring or flavoring matter. In most of these, however, the percentages of alcohol and sugar were less than in extracts prepared according to the Pharmacopoeia, and in some of them considerable amounts of glycerin (maximum 10.76 per cent.) or glucose were present, but these differences bear little or no relation to the value of the product.

All of the U. S. P. and the pure commercial extracts gave with lead acetate a bulky precipitate of a light brown-gray color and a filtrate from this precipitate of a light yellow color.

The adulterated samples contained vanillin in amounts ranging from 0.01 to 0.68 per cent. and nearly all of them contained coumarin in amounts up to 0.23 per cent. The minimum percentage of alcohol was 5.28 and of cane-sugar was 0.47. Glycerin was found in several samples, glucose in one and invert sugar in four. Many of these extracts gave only a slight precipitate with lead acetate, the precipitate as well as the filtrate being dark brown in color. After shaking the filtrate with fullers' earth and again filtering, colorless solutions were obtained in nearly all such cases, indicating that the color was due to caramel. In one extract only was a coal-tar color detected.

CONNECTICUT AGRICULTURAL EXPERIMENT STATION,
NEW HAVEN CONN., July 10, 1902.

[CONTRIBUTIONS FROM THE LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

X. CREAMING OF MILK DURING ITS SALE.

BY WILLIAM FREAR AND M. H. PINGREE.

Received July 25, 1900.

THE theory that the creaming tendency of milk leads to a pronounced separation of this liquid into a fat-rich upper layer and fat-poor lower stratum under the conditions prevailing during the delivery of milk on a wagon-route or during its retailing in the shop, has sometimes been set up as a defense in prosecutions for adulteration of milk by skimming.

The experiments of Wing and Smith[1] satisfactorily show that milk delivered to customers on a wagon-route from a large can by means of a dipper that rests, when not in use, on the bottom of the can, is practically homogeneous. Dean[2] has shown that this is also true of milk that is distributed on a wagon-route, the liquid being delivered from large cans through a faucet.

The range of conditions that may occur during the retailing of milk from a shop, has not been so satisfactorily covered.

Carter Bell[3] examined a sample taken from two gallons of well-mixed milk to establish its initial composition. The milk was then set in a cool place and one pint withdrawn hourly, pains being taken to stir the milk as little as possible during the withdrawal; the total solids and fat in the fractions thus taken varied irregularly to the extent of 0.64 per cent.; there was no important separation of cream at any time; in fact, the last pint was richest in fat.

The writer has recently had occasion to consider the possibilities of separation under the following conditions: The sale of a small quantity of milk, kept in a jar set in a trough of cold water, delivered to customers in portions of a pint to a quart at irregular intervals during a period of six to eight hours, the milk being taken from the jar (without care to stir the contents) by means of a dipper, which is not returned to the jar but laid to one side during the intervals between sales to permit the close covering of the vessel.

In the experiment made to determine the effect of such con-

[1] Cornell Agricultural Experiment Station, Bulletin No. 20.

[2] Ontario Agricultural College, Bulletin No. 66.

[3] *Analyst*, No. 21, December, 1877; cited by Blyth: "Foods," 4th ed., p. 334.

ditions upon the final composition of the milk, a rather deep can was substituted for the jar, otherwise the conditions were exactly as stated above. Two gallons of milk were used, having first been thoroughly mixed and sampled at 8.30 A.M.; at times stated, below, quantities of approximately one pint were withdrawn by a scooping motion of the dipper. The fractions thus withdrawn were analyzed by the usual creamery methods, *i. e.*, the fat was determined by the Babcock test, in duplicate; the duplicates gave identical results in all but two instances, where differences of 0.10 per cent. occurred. The density was determined by use of a Quevenne lactometer, with due correction for temperature variations; the readings were made to one-fifth degree, though the tendency of milk to coat the stem and obscure the scale of the lactometer makes it doubtful whether an accuracy of more than one-half to one-third degree is possible. The total solids were computed from the data thus obtained, by use of the Babcock short formula:

$$\text{Total solids} = \frac{L}{4} + 1.2f,$$

where L represents the Quevenne lactometer reading corrected to 60° F., and f represents the percentage of fat in the milk. Owing to the limitations of the lactometric method mentioned above, it is doubtful whether the solids determinations can be made more closely than 0.08 to 0.12 per cent.

The entire detail of the experiment was carried out by M. H. Pingree.

The results obtained were as follows:

Time.	Fat. Per cent.	Quevenne lactometer readings. (60° F).	Total solids. Per cent.	Solids, not fat. Per cent.
8.30 A.M.....	4.35	34.0	13.72	9.37
10 A.M.....	7.45	31.1	16.69	9.24
11 A.M.....	7.20	32.0	16.64	9.44
12 M.....	6.10	32.8	15.52	9.42
2 P.M.....	5.90	32.8	15.28	9.38
2.30 P.M.....	4.80	33.4	14.11	9.31
4 P.M.....	4.10	34.3	13.49	9.39

It is probable that the lactometer reading at 10 A.M. was slightly too low; otherwise the analytical results check within the allowable limits of error.

The results show very clearly that customers buying the second to sixth portions of milk inclusive, would receive much more than their share of the fat, and the last comers a greatly impoverished milk, when the conditions of sale resemble those of this experiment.

NEW BOOKS.

ON CANE-SUGAR AND THE PROCESS OF ITS MANUFACTURE IN JAVA. By H. C. PRINSEN GEERLIGS. Published in the office of the *Sugar-Cane*, Altrincham.

This book contains brief statements of the chemical compositions of the sugar-cane. In addition to the cane-sugar, which is the principal constituent from a technical standpoint, the sugar-cane consists of water and cellulose or fiber. The fiber is about 70 per cent. pure cellulose and 30 per cent. wood-gum or xylan. The organic acids are glycolic, malic, succinic and small quantities of tannic. Citric, tartaric, and aconitic acids are said by some investigators to exist in normal sugar-cane, but these statements lack confirmation. The lime salts of these organic acids are soluble and are therefore not removed by clarification. From a technical point of view the organic acids which are formed by the action of lime during evaporation of the juices are of quite as much importance as those which exist naturally in the cane. These latter acids are lactic, saccharinic, gluconic, and saccharic. Acetic acid only exists in cane which has undergone fermentation.

The nitrogenous bodies of the cane are chiefly albumen, amides, or amino acids and xanthine bases. It is not certain whether the amides or amino acids consist of asparagine, aspartic acid or glycocol. Xanthine bases are composed chiefly of guanine. The total nitrogen in a mature sugar-cane does not exceed one-tenth of 1 per cent.

The coloring-matters of the cane are chiefly chlorophyll and its alteration products and anthocyan. There is also another coloring-matter in the fiber which becomes yellow on contact with alkaline liquids. The cane wax which exists on the outside of the cane is soluble in alcohol, ether, chloroform and benzine. It is not a wax properly so-called, but a saturated alcohol, having 24 atoms of carbon. In addition to the sucrose, levulose, and dextrose which form the chief part of the soluble carbohydrates, the

cane also contains a small quantity of pectin. The ash of the cane is composed chiefly of potash and silica. Small quantities of soda, lime, magnesia, oxide of iron and sulphuric acid are also found in the ash.

The technical part of the work gives in a condensed form a statement of processes of manufacture which obtain on the island of Java. The articles on clarification, filtration and evaporation will be found useful to those engaged in technical sugar work.

Every one who is engaged in the manufacture of sugar will find Mr. Geerligs's book practical and full of useful suggestions.

H. W. WILEY.

THE GAS ENGINEER'S LABORATORY HANDBOOK. BY JOHN HORNBY. Second edition, revised and enlarged. London, E. & F. N. Spon. New York: Spon and Chamberlain. 1902. xvi + 304 pp.

This volume describes the various analytical operations that are necessary to the proper control of the manufacture of illuminating gas. Parts I, II, and III (112 pages) are devoted to the consideration of elementary quantitative analysis, the topics there discussed being the balance, weights and weighing, sampling, precipitation, filtration, gravimetric determinations and volumetric analysis. Part IV deals with the special analyses required in gas works, such as the analyses of coal and coke, the examination of crude gas, testing of purified gas, analysis of ammoniacal liquor, lime, limestone, oxide of iron, spent oxide and fire-clay, the assay of coal-tar, fractional distillation and the determination of the specific gravity of gases. In Part V, technical gas analysis, calorimetry and the examination of oils are considered. The Appendix contains the English Gas Referees' Instructions concerning the examination of the purity of illuminating gas, and these are followed by various useful tables.

The book contains only what is essentially English practice, and recent improvements in methods and procedures that have been adopted in Germany and in this country have rarely been incorporated by the author. For example, the method for the analysis of coal as recommended in the Report, to the American Chemical Society, of the Committee on Coal Analysis is not even referred to, and the many recent improvements in the methods of analysis of gas mixtures appear to have escaped the author's attention. The work contains, however, much valuable and interesting informa-

tion and will be found a convenient book of reference by those who have to do with the manufacture and analysis of illuminating gas.

L. M. DENNIS.

GUIDE TO PREPARATION WORK IN INORGANIC CHEMISTRY. BY DR. BLOCHMANN; translated by JAS. LEWIS HOWE. Published by Washington and Lee University, Lexington, Virginia. Price, 60 cents.

The translation of Blochmann's "Anleitung zur Darstellung chemischer Präparate" by Professor James Lewis Howe places this excellent little book within reach of students who are unable to read it in the original. While the demand for an elementary text in inorganic preparations is perhaps not so great as it is abroad, inasmuch as many of our texts in general chemistry include considerable work of this nature, nevertheless, too much emphasis can not be placed upon the making of inorganic compounds in exactly the line followed by Blochmann; namely, determining the amount of pure substance which can be made from a given amount of raw material.

Most of the processes given are simple but important, and if faithfully followed out, will give the student a pretty clear idea of the common methods used in making of these simpler inorganic substances. In fact, it would seem that the book might be used to advantage by advanced students of general chemistry before they have had the work in analytical chemistry mentioned by the author.

Several of the first experiments are found in nearly all of our texts on general chemistry, the only difference being that the quantitative results emphasized here, are usually omitted in general chemistry. Among these preparations are hydrochloric acid, nitric acid, ammonia, sodium hydroxide, sodium nitrite, iron sulphate, disodium phosphate and the acids of phosphorus. Among the less common ones are urea, hydroxylamine, crystallized silicon, antimony trichloride and amidosulphonic acid.

While the text is scarcely large enough for a full course in inorganic preparations, it might be used in connection with a course in advanced chemistry with good results. Indeed it is to be hoped that the time will soon come when much of the advanced work in general chemistry will be along the line indicated in this little book.

G. B. FRANKFORTER.

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THE SOLUBILITY EQUILIBRIUM BETWEEN SILVER CHLORIDE, SILVER OXIDE, AND SOLUTIONS OF POTASSIUM CHLORIDE AND HYDROXIDE.

BY A. A. NOYES AND D. A. KOHR.

Received September 15, 1902.

THE theoretical application of the Mass-Action Law and the Ionic Theory to the type of equilibria to which the case named in the title belongs has already been made by Nernst,[1] who also interpreted the well-known results of Guldberg and Waage with barium carbonate and sulphate in accordance with the theory. The principle of the equilibrium is very simple; namely, since

$$C_{Ag^+} \times C_{Cl^-} = S^2_{AgCl}, \text{ and } C_{Ag^+} \times C_{OH^-} = S^2_{Ag_2O},$$

it follows that

$$C_{Cl^-}/C_{OH^-} = S^2_{AgCl}/S^2_{Ag_2O};$$

that is, that the ratio of the concentrations of the chlorine and hydroxyl ions in any solution which is simultaneously saturated with silver chloride and oxide is constant and equal to the ratio of the squares of the solubilities of these two salts in pure water, it being assumed that the two salts are completely dissociated. This principle is of importance not only because it underlies a frequently occurring type of chemical reaction, but also because it

[1] "Theoretische Chemie," Second edition, p. 498.

furnishes an indirect means of determining the solubility in water of salts which are so difficultly soluble that the concentration of their saturated solutions can not be directly determined by analytical methods. We have therefore thought it worthy of further investigation.

An experimental investigation of the analogous principle that applies in the case where one of the difficultly soluble salts is triionic has been made by Findlay,[1] who studied the equilibrium between lead sulphate, lead iodide, and solutions of sodium sulphate and iodide. The theory was found to be confirmed.

Our own investigation consisted in determinations of the solubility in water of silver oxide (and incidentally of silver iodate), and of the concentrations of solutions containing both potassium chloride and hydroxide that are in equilibrium simultaneously with silver chloride and oxide.

The substances used were prepared as follows: Silver oxide was made by precipitating silver nitrate solution with a clear solution of barium hydroxide, and the precipitate was washed by decantation with four liters of freshly boiled water and collected on a filter. The precipitation, washing, and filtration were carried out in an apparatus so arranged that the precipitate did not come at any time in contact with ordinary air containing carbon dioxide. Its purity was established by "rotating" successively the same portion of the oxide with fresh quantities of water, and determining the amount dissolved, which proved to be constant. Silver chloride was prepared by precipitating silver nitrate solution with hydrochloric acid and washing the precipitate thoroughly in a beaker protected from the light. A potassium hydroxide solution was made by dissolving commercial potassium hydroxide "from alcohol" in water, determining analytically the amount of carbonate present, adding the amount of barium hydroxide solution necessary to precipitate it, and decanting the solution after the precipitate had settled. This solution was found to give a faint test for carbonate upon adding more barium hydroxide; but, as it also gave a slight precipitate with sulphuric acid, it was evident that a quantity of barium substantially equivalent to the carbonate had been added. A potassium chloride solution was made from

[1] *Ztschr. phys. Chem.*, **34**, 409 (1900).

salt which had been precipitated by hydrochloric acid and ignited.

The solutions of the pure silver salts in water were saturated by rotating them in a thermostat at 25° for four or five hours in the apparatus described by Noyes.[1] The state of saturation was approached both from the undersaturated and from the supersaturated side. After allowing the solid particles to settle for a short time, the solutions were sucked out of the bottles, which were left standing in the thermostat, through a filter placed in a closed funnel into a 250 cc. graduated flask. The solutions were then precipitated with potassium iodide, about 0.5 cc. of a saturated barium nitrate solution being also added to promote the coagulation. The precipitates were collected in platinum Gooch crucibles upon a layer of finely divided platinum, dried at 160°, and weighed.

The results obtained with silver oxide and with silver iodate[2] are given below. The figures represent the grams of silver iodide obtained from 250 cc. of saturated solution.

TABLE I.

Silver oxide.		Silver iodate.	
From undersaturation.	From supersaturation.	From undersaturation.	From supersaturation.
0.0125	0.0127	0.0109	0.0112
0.0130	0.0120	0.0107	0.0113
0.0125	0.0133	0.0112	0.0117
0.0102[3]	0.0112[3]	0.0108	0.0106
.....		0.0111	0.0114
0.0127	0.0127	0.01094	0.01124

It will be seen that the means of the "undersaturated" and "supersaturated" values agree completely in the case of the silver oxide, and fairly well in the case of the iodate.

The solubilities expressed in mols per liter corresponding to the final means are 2.16×10^{-4} for silver oxide, and 1.89×10^{-4} for silver iodate.

The solubility of the silver iodate was determined with the idea that it might prove a satisfactory salt to use in connection with silver oxide in testing the theory under consideration. But, since

[1] *Ztschr. phys. Chem.*, 9, 606 (1892).

[2] The silver iodate was prepared by precipitating a solution of silver sulphate with one of potassium iodate made from the recrystallized salt. The precipitate was washed thoroughly with hot water.

[3] Omitted in the calculation of the mean.

the solubilities proved to be so nearly identical, and since therefore the ratio of them would not differ greatly from the ratio of their squares, it was decided to combine silver chloride with the silver oxide; and no further work was done with the iodate.

In the first series of experiments with mixed salts, an excess of moist silver oxide and chloride was added to an approximately 1/3 normal solution of potassium hydroxide, and the mixtures were rotated in the thermostat at 25° for a number of hours. In half of the experiments, the mixtures were heated above 25° and shaken, before placing them in the thermostat; but no systematic difference was shown by the results. After the rotation, the solutions were allowed to settle, filtered in the manner above described, and portions of 50 cc. and 200 cc. measured out. The 50 cc. portion was titrated with 0.5217 normal nitric acid[1] to determine the hydroxide present, and was then united with the 200 cc. portion. The whole was then acidified with nitric acid and precipitated with silver nitrate; the precipitated silver chloride was collected in Gooch crucibles, dried, and weighed.

The experimental results and the calculated ratio are given in the following table: The first column contains the number of the experiment; the second, the grams AgCl obtained from 250 cc. of saturated solution; the third, the cubic centimeters of 0.5217 normal HNO_3 neutralized by 50 cc. of saturated solution; the fourth and fifth, the corresponding number of millimols of KCl and KOH respectively per liter; and the sixth, the ratio $C_{Cl'}:C_{OH'}$, calculated in the manner described below.

TABLE II.

Expt. No.	AgCl. Gram.	HNO_3. Cc.	C_{KCl}.	C_{KOH}.	$C_{Cl'}/C_{OH'}$.
1	0.1181	31.60	3.295	329.7	0.01070
2	0.1184	32.10	3.303	334.9	0.01056
3	0.1231	34.30	3.434	357.8	0.01028
4	0.1269	34.35	3.540	358.3	0.01058
5	0.1256	34.20	3.503	356.8	0.01052
6	0.1222	33.50	3.410	349.5	0.01045
			Mean		0.01052

A second series of two experiments (Nos. 7 and 8) was made

[1] This had been standardized through a sodium hydroxide solution against a hydrochloric acid solution in which the acid had been determined by precipitation with silver nitrate.

in which a weaker potassium hydroxide solution (about 0.065 molar) was substituted for the stronger (one-third molar) solution. And in a third series, consisting of four experiments (Nos. 9-12), five times as much solid potassium chloride was added at the start to the potassium hydroxide solution as was present after equilibrium was reached. The results are given in the following table:

TABLE III.

Expt. No.	AgCl. Gram.	HNO_3. cc.	C_{KCl}.	C_{KOH}.	$C_{Cl'}/C_{OH'}$.
7.....	0.0239	6.78	0.666	70.7	0.00995
8.....	0.0190	5.72	0.530	59.7	0.00938
9.....	0.0177	5.20	0.494	54.2	0.00961
10.....	0.0222	6.23	0.620	65.0	0.01006
		Mean.....			0.00975
11.....	0.0375	10.50	1.046	109.5	0.01020
12.....	0.0329	9.05	0.918	94.4	0.01038
		Mean.....			0.01029

It will be seen that the values of the ratio $C_{Cl'}/C_{OH'}$ check fairly well in each set of experiments where the potassium hydroxide concentration was approximately the same. This is true especially of the values of Table II where that concentration and the weight of silver chloride obtained were the greatest. There is a slight decrease in the ratio (from 0.0105 to 0.0098) with decrease of concentration (from 0.35 to 0.06 molar KOH). This is, however, of a secondary magnitude, and the general agreement of the results obtained at different concentrations and by different methods of approaching the equilibrium-condition proves that there can be no considerable error in the results.

A few words must be added in regard to the manner of calculating this ratio. It consisted in first multiplying the concentrations of the two salts given in the fourth and fifth columns of the tables by their respective degrees of dissociation. These last were determined by the following method, which seems to us to be the most exact one for the calculation of the dissociation of salts, in the presence of each other, which do not follow the Mass-Action Law. It is based on the principle demonstrated by solubility experiments,[1] that the concentration of the undissociated part of

[1] See Noyes and Abbott: *Ztschr. phys. Chem.*, 16, 138 (1895).

a salt has the same value, when the product of the concentrations of its ions has the same value, whatever may be the two separate factors of that product. This principle may be applied to the present case in the following manner. In the experiments in Table II the potassium chloride solution is about 0.0033 molar and the hydroxide solution about 0.35 molar. As a first rough approximation we may assume each salt to be 85 per cent. dissociated; and we then get for the product $C_{K^+} \times C_{Cl'}$, the approximate value, $(0.35 + 0.0033) \times 0.85 \times 0.0033 \times 0.85$. The square root of this quantity (or 0.030) is 85 per cent. of the concentration (0.0355) of pure potassium chloride at which the degree of dissociation is the same as it is in the solution of the mixed potassium salts. This degree of dissociation can then be ascertained by reference to a table, or better a plot, of molar-conductivity values. In this case with the help of the data of Kohlrausch and Maltby,[1] it is found to be 90 per cent. In a similar way the dissociation of the potassium hydroxide is found to be 84 per cent.[2] These values are used in calculating the ratios for all six experiments given in Table II. For experiments 7-10 in Table III, the dissociation of the chloride is found to be 95 per cent., and that of the hydroxide 90 per cent. For experiments 11 and 12, the corresponding values are found to be 94 and 88 per cent., respectively.

Adopting for the ratio the round value 0.0100, which is as accurate a conclusion as the experiments admit of, it follows from the equation given at the beginning of this article that the solubility of the chloride should be almost exactly one-tenth $(=\sqrt{0.01})$ of that of the oxide, or 2.16×10^{-5} mols per liter, adopting our analytically determined value for the oxide. The value found by Kohlrausch and Rose[3] by conductivity measurements at 25° was 1.50×10^{-5}. These two quantities are of the same order of magnitude, and to that extent they furnish a confirmation of the theory. Thus, if the fact of the electrolytic dissociation of the two silver salts was not taken into account, it might be expected that the ratio of the solubilities themselves, instead of that of their squares, would be equal to the ratio $C_{Cl'}/C_{OH'}$, and consequently

[1] *Sitzungsber. königl. preuss. Akad. der Wissenschaften*, (1899), p. 665; (1900), p. 1006.

[2] Assuming the limiting value ($\Lambda K + \Lambda OH'$) to be equal to 239 at 18° (Kohlrausch: *Sitzungsber.* just cited, (1901), p. 1031) and using also his data for the higher concentrations.

[3] *Ztschr. phys. Chem.*, 12, 242 (1893).

that the solubility of silver chloride would be 0.216×10^{-4} —an enormous divergence from the result by the conductivity method. It is, nevertheless, true that the deviation of the solubility-ratio directly determined from that predicted from the equilibrium experiments is greater than can, with any degree of probability, be accounted for by the experimental errors, even though these may be considerable in the case of the solubilities of two such difficultly soluble salts. There is, moreover, one explanation of a theoretical nature that would account for the results; namely, the assumption, by no means *a priori* improbable, that silver hydroxide in saturated solution is not even approximately completely dissociated. If Kohlrausch and Rose's value for silver chloride be considered correct and by means of the ratio $C_{Cl'} : C_{OH'}$, the "solubility" of silver oxide be calculated from it, this is found to be 1.50×10^{-4}, while the analytically determined value is 2.16×10^{-4}. The former value which has been considered to be the solubility represents in reality, according to the theory, only the concentration of the dissociated portion in the saturated solution; and, admitting the accuracy of the data, the conclusion might be drawn from them that silver hydroxide in its saturated solution is 70 per cent. dissociated. No independent evidence can be cited, as far as we know, either for or against this conclusion. We have considered the possibility of verifying it by conductivity measurements; but, in view of the difficulties known to exist in the case of such very dilute solutions of bases, it has seemed to be hopeless to obtain sufficiently accurate results, at any rate unless extraordinary precautions were taken, and the matter were made the subject of an extended investigation.

The results of this investigation may be fully summarized as follows:

Solubility determinations at 25°, in which the ordinary methods of analysis were employed, gave for silver oxide 2.16×10^{-4} mols AgOH per liter, and for silver iodate 1.89×10^{-4} mols $AgIO_3$ per liter.

The ratio of the concentrations of the chlorine and hydroxyl ions in solutions of potassium chloride and hydroxide which are simultaneously saturated with silver chloride and oxide increases

only 8 per cent. with a sixfold multiplication of the concentrations of the former salts, and has very nearly the value, 0.0100.

Assuming that the two silver compounds are completely dissociated in their saturated solutions, the requirement of the Mass-Action Law and the Ionic Theory that the ratio of the squares of their solubilities be equal to the concentration-ratio just referred to, leads to the conclusion that the solubility of silver oxide in water is ten times that of silver chloride. The value for silver oxide determined directly by us is, however, 14.4 times that obtained for silver chloride by Kohlrausch and Rose by the conductivity method. It is pointed out that this divergence would be accounted for by the assumption that silver hydroxide in saturated solution is only 70 per cent. dissociated.

An exact method is described of deriving the dissociation of two dissolved salts in the presence of each other, which consists essentially in considering the dissociation of each salt to be that which conductivity measurements show it to have when it is alone present at a concentration of its ions equal to the square-root of the product of the concentrations of its ions in the solution of the mixed salts.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.

SOME NOTES CONCERNING HALPHEN'S TEST FOR COTTONSEED OIL.

BY ELTON FULMER.

Received September 3, 1902.

SINCE Halphen's reaction for cottonseed oil was first published in 1897,[1] it has been submitted to more or less rigid test by a considerable number of investigators. Although some differences of opinion have arisen as to its merits and general applicability, it seems to have been quite generally accepted as the most reliable method at hand for detecting the presence of cottonseed oil in admixture with other oils or fats.

K. Mazher,[2] after using nitric acid, Hirschsohn's reagent, Becchi's test, and Halphen's reaction, concludes that only the latter is to be depended upon.

[1] *J. Pharm. Chim.*, 9, 392 (1897).
[2] *Ibid.*, 17, 159.

J. Wauters[1] reviewed the Becchi test at some length, and concluded that Halphen's reaction is more reliable. He found it to be very delicate, and reported his ability to detect, by its use, 0.25 per cent. of cottonseed oil in a mixture. He also found it possible to determine the approximate amounts of oil in a mixture by comparison with known mixtures. R. D. Oilar[2] gave it extended trial and found it to be reliable for 0.50-0.25 per cent., and that it was even possible to detect such small amounts as $^1/_{10}$ of 1 per cent. Raikow and Tscherweniwanow[3] found it to be sensitive to 0.50 per cent. Many others have found the test as proposed by Halphen to be very satisfactory, and it seems to have great favor among chemists at the present time.

There is, however, some lack of agreement as to its reliability in the case of old or rancid oils.

J. Wauters[4] claims that old oils also respond to the test. P. Soltsien[5] states that the age and rancidity of the oil have no influence upon the characteristic reaction. R. D. Oilar,[6] on the other hand, found that old and rancid oils do not produce the crimson coloration.

The object of this article is not to discuss the sensitiveness nor reliability of Halphen's reaction when applied to normal oils, but rather to call more special attention to two points in connection with its use which require some emphasis. It is manifest that the diagnostic value of the test must be dependent upon all the conditions which affect it. The first point to be considered is the effect of heat upon cottonseed oil in its relation to Halphen's reaction, and the effect of high temperatures upon the palatability of the oil. It is conceded that the substance in the oil to which the characteristic coloration is due, can be eliminated by heat. Whether it is volatilized unchanged, or whether it is decomposed by the heat, is immaterial.

Raikow[7] has shown that the active substances in Becchi's and Halphen's reactions are not identical, and that by oxidation with

[1] *Bull. Assoc. Belg. Chim.*, 10, 404-416 (1899).
[2] *Am. Chem. J.*, 24, 353-373.
[3] *Chem. Ztg.*, 1899, pp. 1025-1026.
[4] *Bull. Assoc. Belg. Chim.*, 10, 404-416 (1899).
[5] *Ztschr. öffentl. Chem.*, 5, 106-107.
[6] *Am. Chem. J.*, 24, 355-373.
[7] *Chem. Ztg.*, 1900, pp. 562-563.

potassium permanganate an oil can be rendered inactive to the latter, while responding with undiminished intensity to the former. This would seem to indicate that the color-producing substance in Halphen's test is easily oxidizable, possibly aldehydic in character, although Gill and Dennison[1] were unable to detect the presence of bodies of this nature in cottonseed oil. But whatever may be the nature of this active substance, it cannot withstand high temperatures. Raikow and Tscherweniwanow[2] found that it was destroyed by heating with superheated steam, or at a temperature of 220° C.

Allen[3] states that oil heated to 245° C. still gives the Halphen reaction but with diminished intensity. Gill and Dennison[4] state, as the result of their own experiments, that when heated to 260° C., an oil will no longer respond to the test. P. Soltsien[5] observes that the reaction still takes place when oil is heated to 200° C., but that a temperature of 250° C. destroys its sensitiveness to the test. D. Holde and R. Pelgry[6] found that a temperature of 200°-210° C. served to lessen the intensity of the coloration produced, and that when oil is maintained at 250° C. for ten minutes, it is no longer capable of producing a color change.

R. D. Oilar[7] concludes from his experimental work that the temperature at which the oil is rendered inactive, depends upon the nature of the containing vessel, and duration of the heating. He found that in glass vessels a temperature of 315°-320° C. was necessary in order to destroy the capability of color reaction, but that the same result was produced by heating the oil for one hour in a steel frying pan, at 140°-150° C.

Some experiments recently carried out in our laboratory showed that a temperature of 265°-270° C. is necessary to render the oil *wholly* inactive. The results given below were obtained with a sample of cottonseed oil which had been sold upon the market for olive oil. It was yellow in color, and had an iodine number of 106.3. It was not in the slightest degree rancid. The tests were

[1] This Journal, 24, 397-398 (1902).
[2] *Chem. Ztg.*, 23, 1025-1028 (1899).
[3] "Commercial Organic Analysis," Vol. II, Part I, third edition, p. 143.
[4] This Journal, 24, 397-398 (1902).
[5] *Ztschr. öffentl. Chem.*, 8, 135-136.
[6] *Chem. Rev. Fett. u. Harz. Ind.*, 6, (4) 67-68.
[7] *Am. Chem. J.*, 24, 355-373.

applied as follows: Eight test-tubes were prepared, each containing 10 cc. of oil, 10 cc. of colorless amyl alcohol, and 10 cc. of carbon disulphide containing 2 per cent. of sulphur. In one tube unheated oil was used; in another, oil that had been previously heated to 180° C. for ten minutes; in the other tubes oil was used which had been heated ten minutes at the following temperatures: 200°, 210°, 220°, 240°, 260° and 280° C. The test-tubes and contents were heated in a bath of glycerol and water to 110° C. for fifteen minutes. Results as follows: The unheated oil gave a deep crimson coloration. That which had been previously heated to 180° C. gave a crimson coloration which was very perceptibly lighter than that given by the unheated oil. There was a gradual lessening of intensity of the color produced by the oil which had been heated to 200° and 210° C., while that which had been submitted to a temperature of 220° C. gave only a light crimson coloration; a slight pink color resulted from the sample heated to 240° C., and only a very faint tinge of pink from that heated to 260° C., while the contents of the tube containing the oil which had been previously heated to 280° C. showed no trace of color.

Soltsien[1] and others believe that cottonseed oil which has been heated to 250° C. is no longer fit for edible purposes. Our work, although by no means disproving this belief, seems to indicate that possibly it is erroneous. The oil was raised gradually to a temperature of 280° C. by us, by heating it in open test-tubes in a paraffin bath. It was kept at this temperature for ten minutes and the only observable difference between it and the unheated oil was an almost imperceptible deepening of the yellow color. At this date, three months after the heating, the heated and unheated samples show no difference in taste or odor. It is probable that oils produced by different methods of extraction and refining may be more or less dissimilar, and hence results from a single sample cannot be regarded as conclusive, although the presumption is strong in favor of the view that oils would differ but little in the characteristic just mentioned. It is, of course, superfluous to remark that if cottonseed oil can be heated to a temperature sufficient to destroy its color reaction without injuring its palatability, Halphen's test cannot be wholly reliable for detecting its presence

[1] *Ztschr. öffentl. Chem.*, 5, 135-136.

when mixed with other oils or fats. However, it is not necessary to completely destroy the capability of color production, and hence not necessary to heat the oil to 265°-270° C., in order to render the test untrustworthy. Heating to 220°-230° C. would be sufficient. This fact brings us to the second point to be emphasized; *viz.*, that the active substance in cottonseed oil to which the characteristic coloration in Halphen's reaction is due, is transmitted apparently unchanged into the fat of animals fed on cottonseed meal.

J. Wauters[1] says that when Halphen's test is applied to butter from cows fed on cottonseed meal, a coloration is obtained equivalent to about 1 per cent. of cottonseed oil. F. Werenskiold[2] is responsible for the assertion that when cows were fed 1 kilo per day of peanut cake, no test for arachidic acid could be obtained in the butter they produced; but that when an equal amount of cottonseed meal was fed, the butter gave a distinct reaction for cottonseed oil with Halphen's reagent.

Allen[3] states that lard and lard oil obtained from animals which have been fed on cottonseed meal, will often respond faintly to Halphen's test. The same statement is repeated by Leffmann and Beam.[4] P. Soltsien[5] stated that he had met with American lards which gave a very weak reaction with Halphen's test, equivalent to about 1 per cent. of cottonseed oil. The same authority reported at a later date[6] that he had obtained a color reaction, also with American lards, equivalent to that given by a mixture containing 25 per cent. of cottonseed oil. The lards in question were obtained by a member of the German Consulate at Chicago, at Armour & Co's establishment, from hogs which had been liberally fed on cottonseed meal. This most astounding result reported by Soltsien has not been corroborated by any other worker. If correct, it almost shakes one's belief in animal metabolism.

In order to satisfy ourselves as to the accuracy of the several statements above quoted, a series of feeding experiments were planned by us so that samples of lard might be obtained from hogs

[1] *Bull. Assoc. Belg. Chim.*, 10, 404-416 (1899).
[2] *Jahresber. öffentl. Veranstalt. Förd. Landw. Norwegen 1. J.*, 1897.
[3] "Commercial Organic Analysis," Vol. III, Part I, third edition, p. 143.
[4] "Food Analysis," p. 169.
[5] *Ztschr. öffentl. Chem.*, 7, 25.
[6] *Ibid.*, 7, 140 (1901).

which had received varying amounts of cottonseed meal as a part of their daily rations. Before we were ready to begin these, it was learned that Director John Fields, of the Oklahoma Experiment Station, was already engaged in a feeding experiment with cottonseed meal, and his cooperation was therefore solicited and secured. The samples of lard mentioned below were rendered from the fat of the hogs he was using in the feeding test, the following details of which were furnished by him. Our thanks are due Director Field for his cooperation. Four lots of hogs were used, each lot containing six animals. All of them had been fed uniformly before the beginning of the experiment, and all of them had received small amounts of cottonsed meal in their ration. The feeding experiment covered a period of fifty-six days, during which time the following rations were eaten:

Lot No. 1.	Lot No. 3.
2026 lbs. wheat chop.	$135\frac{1}{15}$ lbs. cottonseed meal.
Lot No. 2.	$1890\frac{14}{15}$ lbs. wheat chop.
$675\frac{1}{3}$ lbs. wheat chop.	Lot No. 4.
$337\frac{2}{3}$ lbs. wheat bran.	$66\frac{1}{6}$ lbs. cottonseed meal.
1013 lbs. wheat middlings.	$1928\frac{1}{3}$ lbs. wheat chop.

When the animals were slaughtered, a piece of fat about two inches square was taken from each one. Some of the pieces were taken from the head, and some from other portions of the body, but no leaf fat was included. The samples taken from the animals belonging to each lot were mixed and rendered, and the resulting lard sent to us. These lard samples were received and work upon them completed, before receiving any information concerning the rations fed to each lot, and hence our observations were free from any unconscious bias that might have resulted had such information been at hand. The results of our tests are as follows:

	Lot No. 1. Lab. No. 893.	Lot No. 2. Lab. No. 894.	Lot No. 3. Lab. No. 895.	Lot No. 4. Lab. No. 896.
Becchi's test	No reduction	Very slight reduction	Slight reduction	Very slight reduction
Halphen's test	Faint pink	Pink	Light crimson	Light pink
Approximate amount cottonseed oil[1]	1.2%	2.8%	4.0%	2.0%
Iodine number	55.48	59.96	52.96	53.03
Maumené's test: Rise in temp.	25.9°	25.7°	23.5°	26.0°
Maumené's test: Sp. temp. reaction[2]	0.64	0.63	0.58	0.64

[1] Obtained by comparison with known mixtures. [2] Rise in temperature of water, 40.5°.

The cottonseed oil used in the known mixtures for comparison, was the same as previously mentioned. Check tests were made upon lard from animals which had never been fed cottonseed meal, and in no case was the slightest coloration manifested.

These results confirm the observations of others that cottonseed meal will impart the characteristic color-producing power of the corresponding oil, to the fat of animals which eat it. They show a more decided reaction with Halphen's test than indicated by Allen, Wauters, and other authorities quoted, but are very far from corroborating the recent statement of Soltsien. They further show that the color-producing power of the cottonseed oil is very persistent when once introduced into the fat of an animal. Lots 1 and 2 had received no cottonseed meal in their ration for fifty-six days, and yet the lard from their fat showed a coloration with Halphen's reagent equivalent to 1.2 per cent. and 2.8 per cent. of cottonseed oil, lot No. 2 showing even a greater coloration than lot No. 4 which had eaten $66^1/_6$ pounds of cottonseed meal during the feeding period.

We propose carrying on, as soon as practicable, the feeding experiments originally planned, in order to continue our study of the effect of feeding cottonseed meal, upon lard in its relation to Halphen's test.

Summarizing the points above emphasized we have the following:

First.—Cottonseed oil is rendered inactive toward Halphen's reagent by heating to 260°-270° C.

Second.—The intensity of the reaction is very greatly diminished by heating the oil to 220°-240° C.

Third.—It is possible that cottonseed oil may be heated to 280° C. without injuring it, and reasonably certain that a temperature of 220°-240° C. will not render it unfit for use as an article of food, either alone, or as part of a mixture.

Fourth.—Lard from animals fed on cottonseed meal may respond to Halphen's reagent with an intensity of coloration equivalent to several per cent. of unheated cottonseed oil.

It naturally follows from these facts that a mixture of fats or oils may be prepared containing at least 25 per cent. of cottonseed oil which has been heated to 220°-240° C., or a much larger per-

centage if heated to 250°-260° C., which will give a coloration with Halphen's reagent not more intense than that obtained with lard from cottonseed meal-fed hogs. Under such conditions the value of the test for diagnostic purposes is somewhat questionable, especially in its application to the analysis of lard. It is claimed by lard manufacturers and cottonseed oil refiners that the oil is never heated to such a high temperature. This may be true, but it is nevertheless desirable that chemists should be on their guard, and not place too much reliance upon this comparatively new test. For normal, unheated oil, its value is unquestioned; but in view of the facts above discussed, its limitations should not be overlooked.

The analytical work in this paper was performed by Mr. R. W. Thatcher, assistant chemist of the Washington Experiment Station, to whom our thanks are due.

FIXATION OF ATMOSPHERIC NITROGEN BY ALFALFA ON ORDINARY PRAIRIE SOIL UNDER VARIOUS TREATMENTS.[1]

By Cyril G. Hopkins.

Received August 18, 1902.

Many different farmers have tried to grow alfalfa in various sections of Illinois and adjoining states, but, in most cases, it has been pronounced a failure. Where alfalfa has been grown with success in Illinois, it has usually been necessary to sow it on very rich ground or to keep it well manured.

In theory, alfalfa ought to grow and do well on these prairie soils, and it ought not to require heavy and frequent applications of manures, because alfalfa is a very deep rooting crop and is thus capable of drawing upon the soil to great depths for the necessary mineral elements of plant food, and, being a leguminous plant, it has the power of "gathering" nitrogen from the inexhaustible supply of the air, by means of bacteria which inhabit its roots.

Numerous observations made on several fields of alfalfa in different sections of the country during the past few years led the

[1] From advanced sheets of Bulletin No. 76 of the University of Illinois Agricultural Experiment Station.

writer to question whether alfalfa has the power to secure nitrogen from the atmosphere, when grown on these prairie soils. First, because, in nearly every field examined, the plants presented the same peculiar appearance which plants show when grown under artificial conditions *with an insufficient supply of nitrogen.* Second, because, in none of the fields where alfalfa presented this appearance could there be found any tubercles, or nodules, upon the roots of the alfalfa. Third, because liberal applications of barnyard manure produced a vigorous growth and a natural and healthy appearance.

In order to investigate the question, why Illinois soil does not more generally produce good crops of alfalfa, a series of experiments was begun about a year ago. These experiments comprehended the application of various elements of fertility to ordinary black prairie soil, both singly and in combinations, and both with and without the inoculation of the soil with the alfalfa bacteria; that is, with the bacteria which are known to live upon the alfalfa root in other sections of the country. These experiments have been carried on in the pot culture laboratory under controlled conditions and also on plots of ground under field conditions.

POT CULTURE EXPERIMENTS.

The pot culture experiments were planned with a twofold object; first, to test the effect of applying different elements of plant food to the soil to determine the value of such applications for the growing of alfalfa, and, second, to determine the effect upon the growth of alfalfa of inoculating the soil with the bacteria which are able to live upon the roots of alfalfa and gather nitrogen from the air for use of the growing plant.

Applications of Different Elements of Plant Food.

These pot cultures comprise a double set of our regular series of experiments adopted for investigating soils by pot cultures, which is as follows:

Twelve pots are all filled with the soil to be investigated and they are then treated with the following applications:

Pot No. 1—Check. (Nothing applied).

Pot No. 2—Lime.

Pot No. 3—Lime and nitrogen.

Pot No. 4—Lime and phosphorus.
Pot No. 5—Lime and potassium.
Pot No. 6—Lime, nitrogen and phosphorus.
Pot No. 7—Lime, nitrogen and potassium.
Pot No. 8—Lime, phosphorus and potassium.
Pot No. 9—Lime, nitrogen, phosphorus and potassium.
Pot No. 10—Nitrogen, phosphorus and potassium.
Pot No. 11—Check.
Pot No. 12—Check.

The first ten pots really make the complete series. Pots 11 and 12 are extras, or additional checks.

There is a double trial as to the value of an application of lime. First, by comparison between 1 and 2, which shows the effect of applying lime alone. Second, by comparison between 9 and 10, which shows the effect of applying lime after insuring a sufficient supply of each of the elements, nitrogen, phosphorus, and potassium.

Pots 3, 4, 5, 6, 7, 8 and 9 will show the effect of applying to the soil, nitrogen, phosphorus, and potassium, singly and in all possible combinations, and in all cases, after a sufficient quantity of lime has been added to neutralize acidity.

In the following tables and in the photographs, 0 (zero) means no fertilizer; L means lime; N means nitrogen; P means phosphorus; K means potassium (kalium).

Inoculation with Alfalfa Bacteria.

As stated above, two series of pot cultures were made with alfalfa, each of which received the applications of the different elements of plant food as described above. One of these two series of twelve pots each was inoculated[1] with the alfalfa bacteria; the other series was not. In all other respects the two series were treated exactly alike. All of the pots were filled with ordinary Illinois, black, prairie soil, and twenty-five alfalfa seeds were planted in each pot. They were kept in the glass house and were watered with very clear rain-water which was practically free from nitrogen, but which contained a trace of lime dissolved from a new cistern in which it was stored.

1 The inoculating solution was made by shaking 500 grams of soil (obtained from an old alfalfa field in Kansas) with 1000 cc. of water, and allowing it to settle for a few minutes. One cc. of the liquid was used for each alfalfa seed planted.

The pots were all planted in June, 1901. The seeds germinated quite well and a fairly uniform stand was secured in all of the pots. The small plants grew slowly and the different pots showed no very marked differences for several months. A small crop was cut from all the pots in the fall, but they all seemed very much alike and no weights of the cuttings were taken. During the winter the pots[1] showed some marked differences in the growth of the alfalfa and the weights of the cuttings of each pot were taken on March 14, 1902, but they are not reported in this paper.

Another crop was cut from all of the pots on April 23rd and the weights of the alfalfa secured from each pot are given in Table I.

TABLE I.—ALFALFA POT CULTURES; CUT APRIL 23, 1902. WEIGHTS IN GRAMS PER POT AND POUNDS PER ACRE.

Serial No.	Pot No.	Treatment applied.	Green alfalfa. Grams per pot.	Air-dry hay. Grams per pot.	Air-dry hay. Pounds per acre.
1	25	0 :	9	2	320
1	37	0 : Bacteria	37	9	1440
2	26	L :	12	2	320
2	38	L : Bacteria	34	7	1120
3	27	LN :	38	9	1440
3	39	LN : Bacteria	44	10	1600
4	28	LP :	7	1	160
4	40	LP : Bacteria	44	10	1600
5	29	LK :	7	1	160
5	41	LK : Bacteria	32	7	1120
6	30	LNP :	66	16	2560
6	42	LNP : Bacteria	79	19	3040
7	31	LNK :	55	11	1760
7	43	LNK : Bacteria	59	13	2080
8	32	LPK :	7	1	160
8	44	LPK : Bacteria	67	17	2720
9	33	LNPK :	65	16	2560
9	45	LNPK : Bacteria	85	22	3520
10	34	NPK :	68	16½	2640
10	46	NPK : Bacteria	100	20	3200
11	35	0 :	10	2	320
11	47	0 : Bacteria	24	5	800
12	36	0 :	10	2	320
12	48	0 : Bacteria	34	7	1120

[1] The pots used were 10.5 inches in diameter, so that one gram of produce per pot corresponds to one pound per square rod or to 160 pounds per acre. While the exact yield per pot is given in grams in the tabular statement, the computed rate of yield in pounds per acre is also given and this rate of yield is used in the discussion in the text. This is relatively accurate and it is used because we are accustomed to the basis of pounds per acre. Another advantage is that the results from the pot cultures thus become more easily comparable with the actual field results which are given in the following pages.

Effect of Inoculation.

The seven uninoculated pots receiving no nitrogen made comparatively small growth[1] and showed uniformly throughout the period of nearly six weeks the characteristic pale yellowish green color indicative of an insufficient supply of nitrogen. The yields from these seven pots are very small, in no case exceeding the rate of 320 pounds per acre, while 1650 pounds per acre is the average yield of the corresponding inoculated pots. The yield from the inoculated pots ranges from two and a half to seventeen times the yield from the uninoculated pots. For example, the most favored pot receiving no nitrogen (serial No. 8), to which applications of lime, phosphorus, and potassium were made, yielded, when uninoculated, only 160 pounds of hay per acre, while 2,720 pounds per acre was the yield of the corresponding inoculated pot.

The crops produced on the seven uninoculated pots receiving no nitrogen would certainly be pronounced a failure, but the inoculated pots which produced yields from 0.75 to 1.75 tons of alfalfa hay per acre in less than six weeks from the previous cutting give evidence of being a very decided success, considering that this is the third cutting and corresponds to the third clipping in the field, which is frequently too light to pay for saving.

Effect of Nitrogen and Bacteria.

The applications of nitrogen produced a very marked increase in yields, but it is interesting to note that even these artificial supplies of nitrogen had evidently become somewhat depleted by the removal of the previous crops and were no longer sufficient for the greatest possible growth of the alfalfa; and, consequently, in every case where pots receiving nitrogen were also inoculated, a notable increase in growth and yield occurred. In the most favored pots (serial No. 9), to which lime, phosphorus, and potassium were supplied with the nitrogen, this increased yield produced by the bacteria amounted to nearly one-half ton per acre, the uninoculated pot yielding at the rate of 2,560 pounds per acre, while 3,520

[1] It may be observed that the uninoculated pots receiving phosphorus or potassium, or both, with lime, but without nitrogen (4, 5, 8) yielded even less than the uninoculated pots which received lime only or no treatment whatever (1, 2, 11, 12). I know of no explanation for this unless it be found in the fact that the yield of the previous crops from these fertilized pots was larger than from the unfertilized pots and the supply of available nitrogen had been correspondingly reduced.

pounds was the rate of yield of the corresponding inoculated pot.

Effect of Phosphorus.

Applications of phosphorus (or potassium) without bacteria or nitrogen (4, 5, 8) are of no value to the alfalfa.

Phosphorus applied to the inoculated pots or to the uninoculated pots receiving nitrogen produced a very marked increase in yield in every instance. These results confirm the indications observed in the previous crops and prove conclusively that, after provision has been made for a sufficient supply of nitrogen, applications of phosphorus to this soil were greatly to the advantage of the alfalfa crop. For instance where lime and nitrogen alone were applied (3) 1,440 pounds of hay per acre were produced, while 2,560 pounds was the rate of yield where phosphorus was added (6). The treatment: lime, nitrogen, bacteria (3), produced a yield of 1,600 pounds, which was increased to 3,040 pounds by the addition of phosphorus (6). Under the most favorable conditions without phosphorus; that is, with lime, nitrogen, and potassium (7), the yields in pounds per acre were 1,760 and 2,080 without and with bacteria, respectively, and these yields were increased to 2,560 and 3,520 respectively, by the addition of phosphorus (9). The inoculated pot receiving lime and potassium (5) yielded at the rate of 1,120 pounds per acre, but, where phosphorus was added to this combination (8), the yield became 2,720 pounds.

Effect of Potassium.

Applications of the element potassium produced a slight increase in yield when added after sufficient nitrogen was provided (3, 7), but the increase becomes more marked when the potassium is added after both nitrogen and phosphorus have been supplied. For example, with both lime and phosphorus added, and nitrogen accumulated by the alfalfa bacteria, the yield was 1,600 pounds without potassium (4) and 2,720 pounds with potassium (8); and, when an inoculated pot was also given an application of nitrogen (6), it yielded at the rate of 3,040 pounds without potassium and 3,520 pounds with potassium.

It should be remembered that no conclusions can be drawn as to the relative value of applying lime to the soil used because of the

fact that the water used in all of the pots contained a trace of lime.

There is evidence that both phosphorus and potassium have an indirect value aside from their direct value as plant food for the alfalfa. This is the value of these elements to the bacteria. Bacteria themselves are living plants, and while they are microscopic in size they are almost infinite in number, and their multiplication and development are largely dependent upon the supply of available mineral elements of plant food. It will be observed that a yield of 2,080 pounds per acre (7) was secured without the addition of phosphorus. The yield became 3,520 pounds when phosphorus was applied (9). This increase of 1,440 pounds per acre may be due in part to the direct value of the phosphorus to the alfalfa and in part to its value in promoting the development of the bacteria and thus increasing the supply of nitrogen which the bacteria secure from the air and furnish to the growing alfalfa. Again, the addition of phosphorus to the combination, lime, potassium, bacteria, increased the yield from 1,120 (5) to 2,720 (8), an increase of 1,600 pounds per acre. The fact that the soil itself contained sufficient phosphorus to produce a yield of 2,080 pounds (7) tends to prove that the first 960 pounds of this 1,600 pounds' increase was due to the increased development of the bacteria resulting from the additional supply of available phosphorus; the remainder of the increase, 640 pounds, is probably due to both the direct and the indirect value of the phosphorus.

Without addition of potassium the maximum yield was 3,040 pounds (6); consequently the increase in yield from 1,600 pounds (4) to 2,720 pounds (8), resulting from the addition of potassium to the combination, lime, phosphorus, bacteria, was probably largely due to the increased development of the bacteria in the presence of a larger supply of available potassium.

The field experiments, which are described further on, give abundant evidence of the value of applications of lime in promoting the development of the alfalfa bacteria.

The photographic reproduction of the six pots receiving no artificial fertilizer, three of which were inoculated and three uninoculated, as they appeared on May 11th, less than three weeks after cutting off the crops discussed above, may be of interest (see Fig. 1).

Cuttings made from these six pots on May 21st just four weeks after the previous cuttings, gave the results shown in Table II.

TABLE II.—ALFALFA POT CULTURES; CUT MAY 21, 1902. WEIGHTS IN GRAMS PER POT AND POUNDS PER ACRE.

Serial No.	Pot No.	Treatment applied.	Green alfalfa. Grams per pot.	Air-dry hay. Grams per pot.	Air-dry hay. Pounds per acre.
I	25	0 :	7	1	160
I	37	0 : Bacteria	42	12	1920
II	35	0 :	8	2	320
II	47	0 : Bacteria	33	8	1280
12	36	0 :	6	2	320
12	48	0 : Bacteria	33	10	1600

It will be observed that the highest yield of the three uninoculated pots was 320 pounds per acre, while the average yield of the three inoculated pots was 1,600 pounds,—five times as great. These results only serve to confirm those secured from the preceding crops, and to show the value of the inoculation in a most conclusive manner.

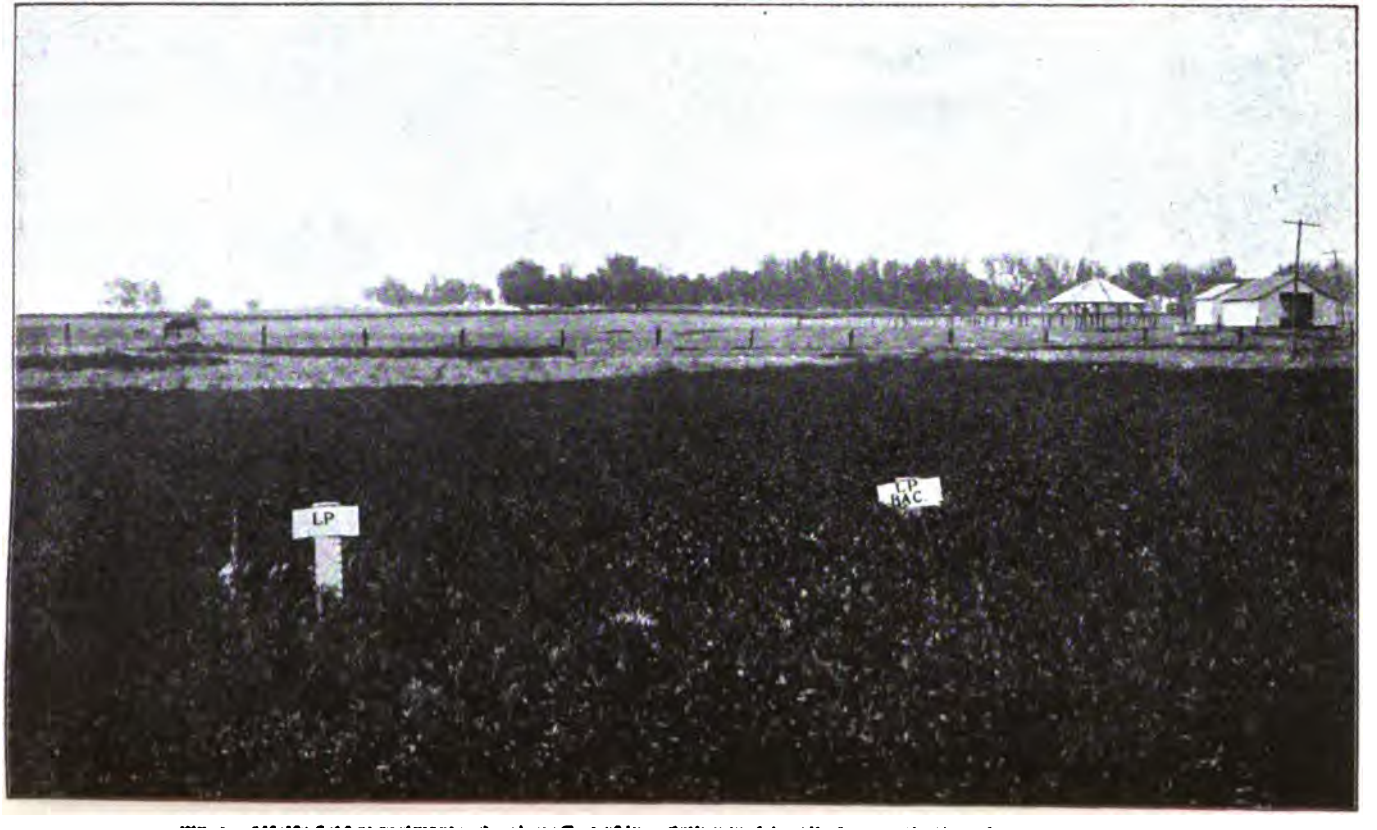
When we remember that the twenty-four pots used in this series of experiments were all filled with the same kind of well-mixed soil, and that this soil is fairly representative of thousands of square miles of black prairie land in Illinois and adjoining states, that both series, of twelve pots each, were kept on the same table in the greenhouse, watered at the same times with exactly the same kind of water, and in every way treated exactly alike, except that one series was inoculated with alfalfa bacteria while the other series was not inoculated, then these most positive and conclusive results, as shown by the records of the experiment, including the color of the foliage, the height of the growing plants, the photographic reproductions, and the absolute yields per pot and rate of yield per acre, seem truly remarkable and appear to be of tremendous importance in solving the question, Why is alfalfa so commonly an unsuccessful crop on ordinary prairie soils?

FIELD EXPERIMENTS WITH ALFALFA.

An acre of ordinary slightly rolling black prairie land, capable of yielding 70 bushels of corn to the acre, was seeded with alfalfa in June, 1901. The soil was considerably better than ordinary cultivated soil (such as was used in the pot culture experiments).



Fig. 1.—Alfalfa pot cultures, showing effect of inoculating ordinary black prairie soil with alfalfa bacteria.


LP
LP
HAC

Previous to 1895, it had been in pasture for at least eighteen years, and since 1897 it had been in meadow; thus, only three grain crops (corn in 1895, 1896, and 1897) were grown on this soil during the past twenty-five years. The field, which was 8 rods wide east and west, and 20 rods long north and south, exclusive of some border and division strips, was divided into two parts by a line running north and south, and into five parts by lines running east and west. The west part of the acre was inoculated with soil taken from an old alfalfa field in Kansas. The five divisions from north to south were fertilized as follows:

Plot No. 1—Check (nothing applied).

Plot No. 2—Lime.

Plot No. 3—Lime and phosphorus.

Plot No. 4—Lime and potassium.

Plot No. 5—Lime, phosphorus, and potassium.

The rates applied per acre were: 320 pounds of air-slaked lime, 320 pounds of bone-meal (containing 30 per cent. phosphoric oxide), and 160 pounds of crude potassium sulphate.

The infected alfalfa soil was applied at different rates of seeding on narrow strips running north and south on the west half of the field, the lightest application (320 pounds) being on the west side, and, on successive strips eastward, the rates of application were 640, 960, 1,280, 1,600, and 1,920 pounds, respectively. Each of these strips was about one-half rod wide. A good stand of young plants was secured, but a very heavy rain storm, which occurred on July 2nd, washed the soil somewhat, and, as the west side of the field was somewhat higher than the east side, it was feared that the bacteria might be carried over the east plots and thus inoculate the whole field to some extent, which afterward proved to be the case, particularly along the east side where the water stood for a short time. The southeast quarter of the field was the lowest part, and, although it was tile-drained, the water stood on it long enough to kill most of the alfalfa plants. Because of these occurrences, the results of the experiment are probably not so marked as they would otherwise have been.

During the summer of 1901, the alfalfa was clipped three times, the clippings being left lying on the field. During midsummer, the weeds seemed to grow faster than the alfalfa, but with each

clipping the alfalfa improved, and in the fall the stand was good where it had not been injured by the water standing on it.

No marked differences were noted among the different plots, excepting that the alfalfa made a much more vigorous growth wherever phosphorus had been applied, the line being very noticeable where the application of phosphorus began.

In the fall, tubercles were found in abundance upon the plants growing in the strips of land where the heaviest applications of infected soil were made, but none were found on plants in the uninoculated soil.

In the spring of 1902 the alfalfa began to grow vigorously and was entirely free from weeds, but within a short time some very marked differences appeared among the different plots. The effect of the inoculation became very apparent, all of the inoculated soil producing a much more vigorous growth than occurred on uninoculated soil, and the more vigorous growth was accompanied by a dark green, healthy-looking color in the growing alfalfa, while the plants on uninoculated soil took on a pale green color indicative of an insufficient supply of nitrogen. This difference in growth and color between inoculated and uninoculated plants was very marked even where no fertilizer was applied, but it was more marked where lime was applied and still more marked where both lime and phosphorus were applied.

Fig. 2 shows the effect of inoculating soil to which both lime and phosphorus had been applied, the inoculated soil producing a markedly increased growth of alfalfa over the uninoculated soil. The label stakes are *two feet* high and serve as a measure of the height of the alfalfa. The difference in thickness of stand can be seen but the difference in color between the inoculated and uninoculated alfalfa is not brought out in the figure. To the southeast may be seen the patch of ground where the alfalfa was destroyed by water, on account of which no results were secured from plots 4 and 5.

Table III gives the yield per acre of air-dry hay from one-thousandth acre plots, the inoculated plots being measured off on the strip where the heaviest application of infected soil was made.

It will be seen that the inoculated plots yielded about twice as much hay as the uninoculated plots.

TABLE III.—ALFALFA FIELD EXPERIMENTS; FIRST CUTTING 1902, MAY 28. WEIGHT IN POUNDS PER PLOT AND PER ACRE.

Plot No.	Treatment applied.	Green alfalfa. Pounds per plot.	Air-dry hay Pounds per plot.	Air-dry hay. Pounds per acre.
1	O :	5½	1 5/16	1313
1	O : Bacteria	11	2 9/16	2563
2	L :	6	1 7/16	1438
2	L : Bacteria	12	2 7/16	2875
3	LP :	7½	1 11/16	1938
3	LP : Bacteria	15	3 5/16	3625

QUANTITATIVE DETERMINATIONS OF THE FIXATION OF ATMOSPHERIC NITROGEN BY ALFALFA WHEN GROWN ON ORDINARY SOIL.

The investigations of Atwater in America, Boussingault and Ville in France, Hellriegel, Willfarth, and Nobbe in Germany, Lawes and Gilbert in England, et al., have fully established the scientific facts: (1) that leguminous plants, as the clovers, peas, beans, vetches, alfalfa, etc., have the power to gather, or accumulate, free nitrogen from the atmosphere; (2) that this fixation of free nitrogen is actually accomplished by microscopic organisms called bacteria which live in little nodules, or tubercles, upon the roots of the legumes; and (3) that, for different species of leguminous plants, there are also different species of "nitrogen-gathering" bacteria. Many investigations have also been conducted to determine the amounts of nitrogen which can be fixed by different leguminous plants, but these experiments have actually been carried on in pure sand cultures under conditions which necessitate that all nitrogen which the legume secures *must* be obtained from the air.

There is abundance of evidence that leguminous plants secure some nitrogen from the air when grown in ordinary soil, if they are provided with the bacteria. Indeed, the presence of the tubercles upon the roots is one of the evidences that free nitrogen is being fixed, and another evidence of that fact is found in the beneficial effects of clover and other legumes in crop rotations. It is a simple matter to determine how much nitrogen is contained in a ton of clover; but, after the amount is determined, it still remains a question as to how much of the nitrogen was taken directly from the soil and how much was secured from the air, and a question very frequently asked is, How much of their nitrogen do legumi-

nous crops obtain from the air and how much do they actually take from the soil?

The pot culture and field experiments described in the preceding pages were conducted on ordinary soil and in such a manner that it can be determined with a high degree of accuracy how much nitrogen was secured from the air by the alfalfa. This is due to the fact that, in all cases, alfalfa was grown not only with bacteria present but also in exactly similar duplicate pots or plots with bacteria absent and the difference between the amounts of nitrogen contained in the crop from the inoculated soil, on the one hand, and in the crop from the uninoculated soil, on the other hand, represents the amount of nitrogen which was secured from the atmosphere by the bacteria. Probably in no case will this amount be larger than the actual truth[1]; but, if the soil which was not intentionally inoculated had nevertheless to some extent become infected with alfalfa bacteria by cross inoculation, then the amount of nitrogen actually secured from the air would be even larger than represented by these determinations.

Fixation of Nitrogen by Pot Cultures.

Table IV gives in pounds per acre the amounts of dry matter and of nitrogen in the crops cut from the pot cultures on April 23, 1902; also the percentage of nitrogen in the dry matter and the

TABLE IV.—FIXATION OF NITROGEN BY ALFALFA IN POT CULTURES; CROPS CUT APRIL 23, 1902.

Serial No	Pot No.	Treatment applied.	Dry matter in crop. Pounds per acre.	Nitrogen in dry matter. Per cent.	Nitrogen in crop. Pounds per acre.	Nitrogen fixed by bacteria. Pounds per acre.
1	25	0 :	280	2.61	7.31	
1	37	0 : Bacteria	1300	4.09	53.17	45.86
2	26	L :	280	3.47	9.72	...
2	38	L : Bacteria	1010	4.24	42.82	33.10
3	27	LN :	1280	4.48	57.31	
3	39	LN : Bacteria	1450	4.48	64.96	7.65
4	28	LP :	140	2.78	3.89	
4	40	LP : Bacteria	1440	4.08	58.76	54.87
5	29	LK :	140	3.59	5.03	
5	41	LK : Bacteria	1010	4.20	42.42	37.39

[1] It is possible, of course, that the inoculated plants might secure somewhat larger supplies of nitrogen from the soil because of their more fully developed root system; but it should still be borne in mind that any such increased root development is due to the inoculation.

Serial No.	Pot No.	Treatment applied.	Dry matter in crop. Pounds per acre.	Nitrogen in dry matter. Per cent.	Nitrogen in crop. Pounds per acre.	Nitrogen fixed by bacteria. Pounds per acre.
6	30	LNP :	2280	4.53	103.19	
6	42	LNP : Bacteria	2780	4.06	112.87	9.32
7	31	LNK :	1570	4.70	73.79	...
7	43	LNK : Bacteria	1890	4.38	82.78	8.99
8	32	LPK :	140	3.15	4.41	
8	44	LPK : Bacteria	2480	3.82	94.74	90.33
9	33	LNPK :	2300	4.09	94.07	
9	45	LNPK : Bacteria	3230	4.00	129.20	25.13
10	34	NPK :	2370	4.14	98.12	
10	46	NPK : Bacteria	2940	4.36	128.18	30.06
11	35	0 :	280	2.63	7.36	
11	47	0 : Bacteria	730	4.34	31.68	24.32
12	36	0 :	280	2.64	7.39	
12	48	0 : Bacteria	1020	4.18	42.65	35.26

amounts of nitrogen per acre obtained from the atmosphere by the alfalfa bacteria in the inoculated pots.

Where neither nitrogen nor bacteria were added to the soil, all of the nitrogen removed in the crops[1] must have been derived from the original soil. In the three series of pots receiving no fertilizers (1, 11, and 12) the crops from the uninoculated pots contained 7.31, 7.36, and 7.39 pounds of nitrogen per acre, respectively, while 53.17, 31.68, and 42.65 pounds of nitrogen in the crop are the respective rates per acre of the corresponding inoculated pots. The average of these is 42.50 pounds for the three inoculated pots and 7.35 pounds for the three uninoculated pots, making an average difference of 35.15 pounds in favor of inoculation. In other words, as an average of three separate determinations, with no application of plant food, the bacteria "gathered" and "fixed" and furnished to the growing alfalfa more than 35 pounds of nitrogen per acre. At the present average price for nitrogen in commercial fertilizers (15 cents a pound) these 35 pounds of nitrogen are worth $5.25.

The addition of potassium without phosphorus (5) gave no in-

[1] The amounts of nitrogen given may possibly be too high for some of the uninoculated pots, because of some cross inoculation. The inoculated and uninoculated series of pots stood side by side on the same table, and either spattering of water or more likely the carrying of infected soil by ants (which were frequently found in the pots) or other insects, finally transferred some bacteria to the uninoculated series, which fact became evident, later in the season of 1902, by the development of tubercles, and the markedly increased growth of an occasional plant in the uninoculated pots.

crease in the amount of nitrogen fixed. With phosphorus added to the soil (4), the nitrogen in the crop was increased by the presence of the bacteria from 3.89 pounds to 58.76 pounds per acre, 54.87 pounds of nitrogen per acre having been fixed by the bacteria.

Under the most favorable conditions, when both phosphorus and potassium were applied (8), still more marked results were obtained, the nitrogen in the crop having been increased from 4.41 to 94.74 pounds per acre by the bacteria; that is, the bacteria gathered nitrogen from the air at the rate of more than 90 pounds per acre, which was utilized by the growing alfalfa. At market prices, the nitrogen gathered is worth $13.50 per acre.

It is of interest to observe that even in the pots to which applications of nitrogen had been made (3, 6, 7, 9, 10) some nitrogen was fixed when the soil was inoculated, ranging from 7.65 pounds per acre (3), with no addition of phosphorus or potassium, to 25.13 and 30.06 (9 and 10) pounds per acre under the most favorable conditions, with applications of all mineral elements.

Usually small immature plants contain much higher percentages of nitrogen than do more fully developed plants, but it will be seen from Table IV that, without exception, the heavy crops of alfalfa contained much higher percentages of nitrogen than the lighter crops. Triplicate determinations of nitrogen in the crops from unfertilized pots (1, 11 and 12) showed 2.61 2.63 and 2.64 per cent. of nitrogen in the dry matter from uninoculated pots yielding only 280 pounds of dry matter per acre, and 4.09, 4.34, and 4.18 per cent. of nitrogen in the dry matter from the inoculated pots with an average yield of more than 1,000 pounds per acre. A similar effect was produced in all cases, whether nitrogen was added as a nitrogenous fertilizer or gathered by the bacteria,—all of which tends to prove that, with insufficient nitrogen, the plants make as much growth as possible until the fixation of carbon is practically stopped by the lack of nitrogen, as indicated by the pale yellowish green color of the foliage.

Table V shows the data relating to the fixation of nitrogen from the next cutting (May 21st) of the six unfertilized pots (1, 11, 12), three of which were inoculated.

TABLE V.—FIXATION OF NITROGEN BY ALFALFA IN POT CULTURES; CROPS CUT MAY 21, 1902.

Serial No.	Pot No.	Treatment applied.	Dry matter in crop. Pounds per acre.	Nitrogen in dry matter. Per cent.	Nitrogen in crop. Pounds per acre.	Nitrogen fixed by bacteria. Pounds per acre.
I	25	O :	140	2.69	3.77	...
I	37	O : Bacteria	1720	3.52	60.60	56.83
II	35	O :	280	2.47	6.91	
II	47	O : Bacteria	1170	3.69	43.18	36.27
12	36	O :	280	2.61	7.31	
12	48	O : Bacteria	1460	3.66	53.48	46.17

These results only confirm those of the previous cutting and show that on ordinary unfertilized Illinois soil the alfalfa bacteria were capable of fixing 46.42 pounds of nitrogen per acre, as the average of the three separate determinations.

The average percentage of nitrogen in the dry matter of the crops from the three uninoculated pots was 2.59, while 3.62 is the average percentage from the three inoculated pots.

Fixation of Nitrogen in Field Experiments.

Table VI gives the same data for the field experiments as are given in Tables IV and V for the pot cultures. These determinations were made on the crops cut from the exact thousandth-acre plots on May 28, 1902.

TABLE VI.—FIXATION OF NITROGEN BY ALFALFA IN FIELD EXPERIMENTS; CROPS CUT MAY 28, 1902.

Plot No.	Treatment applied.	Dry matter in crop. Pounds per acre.	Nitrogen in dry matter. Per cent.	Nitrogen in crop. Pounds per acre.	Nitrogen fixed by bacteria. Pounds per acre.
I	O :	1180	1.85	21.81	
I	O : Bacteria	2300	2.70	62.04	40.23
2	L :	1300	2.02	26.20	
2	L : Bacteria	2570	2.65	68.02	41.82
3	LP :	1740	2.03	35.40	
3	LP : Bacteria	3290	2.71	89.05	53.65

These results secured under field conditions on good black prairie soil are in perfect agreement with the results from the pot culture experiments, the amount of atmospheric nitrogen fixed by the alfalfa bacteria being 40.23 pounds per acre on the unfertilized plot, 41.82 pounds on the limed plot, and 53.65 pounds per acre on the plot receiving both lime and phosphorus. Almost two-thirds

of the total nitrogen contained in the crop from the inoculated unfertilized plot (1) was secured from the atmosphere by the alfalfa bacteria. It should be borne in mind that nitrogen is required for root growth as well as for growth above ground and also that these amounts were obtained from a single crop of alfalfa, and that three or four crops will be cut during the season. From the data already given, it will be seen that on the unfertilized soil four such crops as that cut on May 28th from the inoculated plot would mean at least 160 pounds of atmospheric nitrogen fixed by an acre of alfalfa during a single year, and this would require a total yield of only about five tons of alfalfa hay for the season, which is by no means a maximum yield for alfalfa on Illinois soil under the most favorable conditions, as has been shown in the preceding pages.

The percentage of nitrogen is much higher in the crops from the inoculated plots, the average being 1.97 per cent. in the dry matter for the uninoculated plots and 2.69 for the inoculated plots. This means, of course, that the hay produced on the inoculated plots is not only more in quantity, but it is also much better in quality, the percentage of protein averaging only 12.29 in the dry matter of the uninoculated crops, while 16.84 is the average percentage for the inoculated plots.

UNIVERSITY OF ILLINOIS AGRICULTURAL EXPERIMENT STATION.

THE IDENTIFICATION AND COMPOSITION OF MALT LIQUORS.[1]

BY CHARLES LATHROP PARSONS.

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THREE of our northeastern states have laws which, if enforced, strictly prohibit the sale of all intoxicating liquors and of some which are, perhaps, not intoxicating. In two of these States the statutes use the phrase "Malt Liquors" of any kind, and prosecutions have been brought in large numbers under this section. To obtain convictions, therefore, it has been necessary to convince the judge or jury that the beer in question was brewed

[1] Read at the Pittsburg Meeting of the American Chemical Society.

in part, at least, from malt, for it has quite properly been held in the lower courts that a malt liquor is one which has had germinated grain or some preparation of malt used in its brewing. The question, therefore, submitted to chemists has not been the simple one of alcohol content.

In looking over the literature of the subject almost nothing will be found bearing on this phrase of the question. Much has been written on the essential constitution of pure malt liquors and many analyses have been made to prove that certain beverages were up to standard and that foreign substances had not been used in their preparation. Here, however, it is not to find adulteration but to prove positively that the main source of a first quality beer was used. This would perhaps seem easy from appearance alone but there are beers on the market in these States, with the main physical properties of lager or ale, which analyze quite differently from the pure malt liquors and the representative of at least one of the manufacturers has frequently taken oath that absolutely no malt or preparation of malt was used in their manufacture. The point at issue becomes then very much the same as if the chemist was asked to prove, by analysis, that oleomargarine contained no butter and, if the amounts of malt or butter are small, the solution in either case is, at the present time, equally impossible. The claim has been made that maltose is a characteristic which, if found, would satisfy the meaning of a malt liquor but the contention has naturally met with about as much success as if the presence of butter in oleomargarine was claimed because stearine was present.

If we try to find any one constituent of malt which is absolutely characteristic of that substance and which will be unchanged in the finished beer we immediately encounter difficulties. Diastase, formed in the germinating grain, is destroyed when the beer wort is boiled previous to its fermentation. Maltose and dextrine are large constituents of the glucose which, as the analyses to follow will indicate, and as most brewers admit, is now quite generally used in brewing. Alcohol can arise from sugar of any kind. Sykes,[1] Osborne,[2] Osborne and Campbell,[3] E. Erich,[4] and H.

[1] Transactions Institute of Brewing, 4, 173 (1891).
[2] *Am. Chem. J.*, 17, 429. 539 (1895).
[3] *Ibid.*, 18, 542.
[4] *J. Soc. Chem. Ind.* (1896), p. 366.

Schjerning[1] have given much careful study to the various albuminoses, proteoses, etc., of grain, malt and beer wort but none of these substances appears to persist in an unchanged form in the beer, so that its individual presence could be used as a proof of its source. The bitter principle present has no bearing on the case. The extended investigations of O'Sullivan published in the Journal of the Chemical Society and elsewhere throw no light on this problem. The study of the spectra of the coloring-matter of malt by H. C. Sorby[2] shows it to be characteristic but again it is much modified in beer and, while this field seems worthy of exploration, has not been sufficiently investigated.

Grain and sugar of some form, generally glucose, are the only forms of malt substitutes from which beers are brewed. Of the various sugars used, all have one characteristic in common in that they contain little or no nitrogenous matter or phosphates. Also, while glucose has a considerable and varying amount of ash it is of a distinctly different character from that derived from malt. On the contrary, we have in grain of any kind the essential constituents of malt with the exception of diastase. Fortunately grain can only be used in brewing when mixed with malt in order that the necessary diastase may be furnished. Therefore it may be considered as malt in determining whether or not the beer under examination was a malt liquor. The ash of grain, malted or unmalted, is rich in phosphorus and potassium and poor in sulphates. The ash of glucose is poor in the first-mentioned constituents but is usually rich in sulphates. The nitrogenous matter, the phosphates, which are also characteristic of seed products, and many of the constituents of the ash are conveyed in quite considerable quantities to the beer and give it its chief nutritive value. The beers which are claimed to be brewed mainly from glucose show, on analysis, little nutritive value. This is to be expected if the claims are true. The hops carry some of the above constituents in both cases to the beer. Also I am told by the manufacturer of the only really successful imitation malt liquor on the market, which is claimed to use glucose as its sole source of alcohol, that they are obliged to add some soluble "French albumin" in order to get their yeast to work and that then, although they

[1] *Ztschr. anal. Chem.*, **38**, 285 (1896).

[2] *Deut. Viertel. Jahreschrift. offenl. Gesundhtspflg*, II, Heft 1.

boil off part of the alcohol and at the same time Pasteurize the beer, they have great difficulty in preserving it for any great length of time.

The following summary of 172 samples of American lager and 199 samples of American ale, published by Dr. F. E. Englehardt in the Report for the New York Board of Health for 1886 and taken in part from Bulletin 13, part 3, U. S. Department of Agriculture, Division of Chemistry, give a good idea of the average composition of the commercial malt liquors of this country as they were made eighteen years ago.

COMPOSITION OF 172 SAMPLES OF AMERICAN LAGER BEER.

	Sp. gr.	Alcohol by volume.	Extract.	Ash.	Phosphoric acid (P_2O_5).
Average	1.016	4.70	5.86	0.259	0.096
Maximum ..		8.78	9.64	0.412	0.120
Minimum ...		0.85	3.65	0.172	0.050

COMPOSITION OF 199 SAMPLES OF AMERICAN ALE.

Average	1.013	5.77	5.42	0.307	0.083
Maximum ..		11.16	9.50	0.552	0.166
Minimum ...		3.02	2.70	0.197	0.0405

Further an average of 28 samples of American malt liquors analyzed by Dr. C. A. Crampton[1] shows the following composition:

COMPOSITION OF 28 SAMPLES OF AMERICAN MALT LIQUORS.

	Sp. gr.	Alcohol by volume.	Extract.	Ash.	Albuminoid (N × 6.25).	Phosphoric acid (P_2O_5).	Reducing sugars as maltose.	Dextrine.
Average ..	1.0161	5.79	5.53	0.279	0.563	0.077	1.65	2.33
Maximum	1.0241	8.63	8.19	0.472	0.763	0.104	2.67	3.12
Minimum.	1.0077	4.85	3.46	0.183	0.400	0.056	0.59	0.90

These analyses are all characterized by notable quantities of albuminoids and phosphates, the lowest amounts being 0.400 and 0.0405 per cent. respectively while the averages are about 0.563 and 0.085 per cent. The larger the quantity of glucose used, the lower, relatively, will be the amounts of nitrogenous and phosphatic material. My own experience leads me to believe that no true lager or ale on the market as such will be found to contain less than 0.04 per cent. of phosphoric acid and 0.25 per cent. of albuminoids, even when these facts are taken into consideration. An amount of glucose equivalent to from 15 per cent. to 20 per

[1] Division of Chemistry, Bulletin 13, Part 3.

cent. of the mashing material appears to be about the maximum quantity used even with the poorest beers derived from malt. König, in his *Menschliche Nahrungs u. Genussmittel,* gives 0.05 per cent. as the minimum amount of phosphoric acid allowable in a beer containing 5 per cent. of extract or over, while the Association of Bavarian chemists[1] gives the minimum amount of albuminoids as 4 per cent. of the extract. It will be seen from the above-quoted analyses and those to follow that their figures are lower than will probably be found in an American malt liquor, even with a considerable proportion of glucose used.

As a further contribution to the literature of this subject I think it will be well to offer the following summary of 76 analyses of beers recently made by me, each of which I considered to give sufficient evidence to warrant a chemist in pronouncing them to have been brewed from malt. This judgment would rest largely upon their percentage of albuminoids and phosphoric acid but is supplemented by the composition in general.

COMPOSITION OF 76 SAMPLES OF AMERICAN MALT LIQUORS.

	Sp. gr.	Alcohol by volume.	Extract.	Albuminoid (n × 6.25).	Phosphoric acid.	Ash.	Sulphates in ash.	Free acid.
Average ..	1.0100	5.61	4.61	0.470	0.061	0.209	6.34	0.26
Maximum	1.0210	7.85	7.64	0.614	0.095	0.296	12.67	0.87
Minimum.	1.0047	0.35	3.15	0.290	0.045	0.147	2.44	0.10

Approximately 50 per cent. of these malt liquors contained salicylic acid.

A glance over this last summary will show at once that the beers analyzed are not equal in quality to those whose analyses have been before quoted. The high percentages of sulphates, the comparatively low specific gravity and extract, point to a much more general use of glucose than formerly existed. This question of quality was also frequently apparent in the physical properties of the beer and it would be a curious thing to know whether or not their sale in so-called prohibition States had anything to do with this quality. In one or two instances only have I any knowledge of the brands.

The average high percentage of free acid shows that some of these beers reached me in anything but the best of condition and the percentages of alcohol were probably modified from the

[1] Bulletin 13, Department of Agriculture, Division of Chemistry, Part 3.

original in many instances. The alcohol is reported in per cent. by volume for the reason that it is the volume per cent. which is usually the legal one. The per cent. of albuminoids and phosphoric acid, is, however, unmodified from that of the perfectly fresh beer for when any yeast was present the container was thoroughly shaken before the sample was taken and the contents of the yeast, which had been derived from the beer, included in the results. It is particularly worthy of note that in some samples not included above, where the alcohol had been wholly changed into acetic acid, the special characters derived from the malt still stood calculated. While the above summary of analyses shows some interesting facts the mistake should not be made of using it as a basis of judging the composition as a whole of fresh American beer and ale. They indicate more closely the kind of material that is apt to be sent to a chemist as the result of a police seizure—material which is sometimes kept several days or even weeks before reaching his hands. If, however, the sample can be treated, when first taken, with eight to ten drops of formaldehyde to the liter of beer, it will keep it in excellent condition, for analytical purposes, for weeks.

If a beer shows the composition given in the analyses already quoted it can safely be pronounced a malt liquor. The converse is not necessarily true. A beer might have had a small amount of malt used in its production and the fact be absolutely undeterminable. In such case, and that is probably just the case with many of the "temperance beers" on the market, chemists can say only "no evidence of malt." The analyst can only be sure of his statements that malt was used when a considerable proportion of that material was used in the brewing. Fortunately the "no malt" beers which have come under my own observation do not even approach the composition of the ordinary part glucose beer.

The following are typical analyses of beer which in my opinion do not furnish sufficient evidence in warranting a chemist in stating that they were brewed from malt.

No.	Sp. gr.	Alcohol by volume.	Extract.	Albuminoid (n × 6.25).	Phosphoric acid.	Ash.	Sulphates.	Free acid.
1	1.0074	1.68	2.52	0.114	0.010	0.19	21.22	normal
2	1.0098	2.63	3.40	0.215	0.023	0.189		normal
3	1.0062	2.27	2.25	0.150	0.015	0.124	11.30	normal
4	1.0112	2.11	3.53	0.133	0.015	0.140	10.81	normal
5	1.0041	1.85	1.73	0.031	0.010	0.088	12.50	normal

The percentages of sulphates are high but a glance at the previous table will show at once that too much dependence must not be placed upon this fact. It is simply circumstantial evidence.

The composition of the ash of beers is of great importance in doubtful cases but unfortunately a complete analysis of ash is tedious and would make undesirable expense. Its actual amount tells but little, its composition being the important consideration. Unfortunately, also, more beer is required to obtain enough ash for analysis than is generally sent to the analyst. Blyth[1] gives the following average composition of beer ash:

I have made but one fairly complete ash analysis of any one of the above samples, that of No. 5 of the "no malt" beers, which I place beside that of Blyth's for comparison.

	Malt beer (Blyth).	"No malt" beer (Parsons).
K_2O	37.22	12.93
Na_2O	8.04	19.61
CaO	1.93	undetermined
MgO	5.51	"
Fe_2O_3	trace	"
SO_3	1.44	10.81
P_2O_5	32.09	10.71
Cl	2.91	21.76
SiO_2	10.82	7.50

The differences are very prominent and would be a great help in pronouncing judgment. Here again would arise the same difficulty as before, if only small amounts of malt had been used and the verdict would probably always be in accord with that rendered by the albuminoids and phosphoric acid.

METHODS OF ANALYSIS.

Specific Gravity.—Official method.[1] Pycnometer with thermometer stopper used.

[1] "Foods," Fourth edition, p. 518.

[2] Bulletin No. 65, Department of Agriculture, Bureau of Chemistry.

Alcohol.—Pycnometer with thermometer stopper. Pycnometer carefully calibrated with distilled water at 15.6°, 17°, 20°, and 22° C., according to temperature of atmosphere. Alcohol solution weighed at same temperature. The departure from 15.6° may be criticized but a study of the coefficients of expansion of pure water and mixtures of alcohol and water[1] will show that with such dilute solutions of alcohol as are under consideration the error would be less than 0.01 per cent. This is less than would result from evaporation due to capillarity around the ground-glass stopper if the pycnometer is filled at 15.6° and brought to room temperature to avoid condensation on the glass, is much less than would arise from the use of a hydrometer, even the most delicate made, and is fully as accurate as by calculation from the tables of Squibb. When distinctly acid, the beer was, of course, always neutralized before distillation.

Extract.—Provisional official method,[2] using the formula 1—sp. gr. (of alc. dist.) + sp. gr. (of beer) and using the tables of Oestermann and Schultze. Many comparative results were made by evaporation and by direct determination of the specific gravity of the dealcoholized beer. The results from the use of the tables never varied greatly from the others and are probably much nearer correct owing to the hydrolysis of sugar in the first case and the precipitation of albuminoids, etc., in the second.

Albuminoids (total $n \times 6.25$).—Official Gunning method, with the additional precaution of always first boiling down the beer taken to a small bulk, but not to dryness, after acidification with a few drops of sulphuric acid, before the main quantity of acid or potassium sulphate was added. This did away with the foaming which was otherwise uncontrollable.

Phosphoric Acid.—Uranium acetate method. Solution of uranium acetate in which 1 cc. was equivalent to 0.01 per cent. P_2O_5 when 50 cc. of beer were used. When the beer was light-colored the method was applied both to the beer itself and to the ash; otherwise to the ash alone. The results on the ash were generally 0.1 or 0.2 cc. higher than on the beer itself and sometimes even more when any considerable quantity of yeast had

[1] See Makins: *J. Chem. Soc.*, 99, 224; Silbermann: *Compt. rend.*, October, 1848.
[2] Bulletin No. 65, Bureau of Chemistry.

developed. Results were compared with the molybdate method and agreed closely. There was no difficulty in determining the point of precipitation of the phosphate within 0.1 cc. when the ash was used. The ash was moistened with concentrated hydrochloric acid and the acid evaporated on the water-bath. It was then boiled with 50 cc. of distilled water and titrated with uranium solution. Under these conditions the end-point was always sharp. If the ash was not treated with hydrochloric acid, if acetic acid was substituted for hydrochloric acid or if, after treatment with hydrochloric acid, the ash was heated much above the temperature of boiling water, the phosphates were insoluble or, at least, remained in a form where they were not attacked by the uranium solution. With these precautions, the uranium method gives on a beer ash results which are quite accurate to 0.1 cc., and which are quickly obtained.

Sulphates.—The photometric method of Hinds[1] was used. In my hands his tables give percentages in beer ash more closely agreeing with the gravimetric than when the tables of Jackson[2] were used, as the latter yielded too high results. The solution of ash in hot, dilute hydrochloric acid, was either taken direct after filtering, or the filtered solution from the phosphoric acid determination could be equally well used.

Ash, Salicylic Acid, and Free Acid were determined by the usual official methods.

NEW HAMPSHIRE COLLEGE,
July 2, 1902.

ON AZOXYBENZENE.

Received September 3, 1902.

BY ARTHUR LACHMAN.

A FEW years ago, I endeavored to deduce the structure of the nitro-group, and came to certain conclusions.[3] Subsequent developments, however, showed the line of reasoning then adopted to be erroneous; and these conclusions have since been withdrawn.[4] A new method of investigation became necessary, and a

[1] This Journal, 22, 269.
[2] *Ibid.*, 23, 799.
[3] *Am. Chem. J.*, 21, 433 (1899).
[4] This Journal, 23, 897 (1901).

study of azoxybenzene, one of the reduction-products of nitrobenzene, seemed to promise useful results. The present paper deals with the properties and the structure of azoxybenzene.

Azoxybenzene stands in a peculiarly intimate and important relation to nitrobenzene. First of all, in its general indifference to all but reducing agents, it closely resembles its mother-substance. Secondly, it still contains oxygen, and has no hydrogen directly attached to its nitrogen atoms. Thirdly, it is always the first, and usually the chief, product of alkaline reducing agents upon nitrobenzene. In view of this important relationship between these two substances, it is curious that so little is known about azoxybenzene. Its natural history is exceedingly meager.

Azoxybenzene was first prepared by Zinin,[1] by the action of alcoholic potash on nitrobenzene. Klinger, at a much later date, investigated the action of different alcohols and alkalies upon aromatic nitro-compounds,[2] and for the preparation of azoxybenzene itself recommended the method still in common use,—reduction of nitrobenzene with a solution of metallic sodium in methyl alcohol. Various other reducing agents have at times been proposed, such as alkaline stannites, sodium amalgam, etc.; but they do not give good yields with nitrobenzene, so far as I have tried them.

The chemical reactions of azoxybenzene have not been exhaustively studied. Mild reducing agents, *e. g.*, metallic iron,[3] remove oxygen, and leave azobenzene; more energetic agents reduce azoxybenzene to aniline, whereby hydrazobenzene[4] often appears as an intermediate product. Aside from these more obvious reactions, only one has attracted more than a passing interest. When azoxybenzene[5] is warmed with concentrated sulphuric acid, it is isomerized to *p*-hydroxyazobenzene:

$$C_6H_5—N_2O—C_6H_5 \rightarrow C_6H_5—N=N—C_6H_4OH.$$

The mechanism of this reaction, which has not yet been satisfactorily explained, will be discussed below.

The data which I have gathered during my study of azoxybenzene are here presented under the following heads:

[1] *J. prakt. Chem.*, 36, 98 (1845).
[2] *Ber. d. chem. Ges.*, 15, 865 (1882); 16, 941 (1883).
[3] Schmidt and Schultz: *Ann. Chem.* (Liebig), 207, 328 (1881).
[4] *Cf.* Meyer-Jacobson: "Lehrbuch," II, p. 251.
[5] Wallach: *Ber. d. chem. Ges.*, 13, 525 (1880); 14, 2617 (1881).

I. The preparation of azoxybenzene.
II. The action of sulphuric acid on azoxybenzene.
III. *p*-Hydroxyazobenzene-*p*-sulphonic acid.
IV. Miscellaneous reactions of azoxybenzene.
V. Some reactions of diphenylnitrosamine.
VI. The constitution of azoxybenzene.

I. THE PREPARATION OF AZOXYBENZENE.

The reduction of nitrobenzene to azoxybenzene is best accomplished by the use of alcohols in alkaline solution. As mentioned above, Zinin used ordinary alcohol and caustic potash. This gives a rather impure azoxybenzene and an imperfect yield. Klinger obtained better results with sodium methylate dissolved in methyl alcohol. The use of metallic sodium in large quantities, however, I found to be inconvenient as well as expensive, for the sodium must be added slowly to the alcohol. A remark of Klinger's, that ordinary methyl alcohol often contains *much water*, suggested the direct use of sodium hydroxide; and it was soon found that a return to Zinin's method, simply changing alkalies and alcohols, gave much the best results.

It was also found, however, that to obtain good yields of azoxybenzene it is essential for the methyl alcohol to be absolutely ketone-free, whereas the amount of water present is relatively without influence. In all the following experiments, the reagents (sodium hydroxide, methyl alcohol, nitrobenzene) were directly mixed, and gently boiled for three hours on a water-bath, a previous test having shown that a separate solution of the alkali before adding nitrobenzene had no influence upon the course of the reaction.

INFLUENCE OF WATER UPON YIELD OF AZOXYBENZENE.

Methyl alcohol acetone-free. cc.	Water. Per cent.	Sodium hydroxide. Grams.	Nitrobenzene. Grams.	Yield of azoxybenzene. Per cent.
800	4	160	120	83
200	8	40	30	75
200	13	40	30	83

In all three cases, the azoxybenzene was of a bright yellow color, and practically pure.

INFLUENCE OF ACETONE UPON YIELD OF AZOXYBENZENE.

Methyl alcohol. cc.	Acetone. Per cent.	Sodium hydroxide. Grams.	Nitrobenzene. Grams.	Yield of azoxybenzene. Per cent.
400	3	80	60	62
650	none	120	100	97
1000	none	200	150	95
650	2.7	120	100	62

In the first and fourth experiments, the azoxybenzene was dark brown, and contained aniline, unaltered nitrobenzene, and isonitrile.

Upon the basis of the above results, the preparation of azoxybenzene is a simple matter. Boil a mixture of 1000 cc. acetone-free methyl alcohol, 200 grams sodium hydroxide and 150 grams nitrobenzene for three hours; distil off the alcohol, and pour the residue into cold water. Freeze the precipitated yellow oil in ice, and wash with water until free from alkali. Then melt the crystals in a little dilute hydrochloric acid to remove traces of aniline, freeze again, and wash free from acid. The resulting crystalline mass is crushed and dried in air, and is now sufficiently pure for nearly all purposes. Azoxybenzene may be recrystallized from alcohol or from ligroin.

SOLUBILITY OF AZOXYBENZENE IN LIGROIN (b. p., 70°-80°).

100 grams ligroin will dissolve at 0° 10.7 grams azoxybenzene.
100 grams ligroin will dissolve at 15° 43.5 grams azoxybenzene.

SOLUBILITY OF AZOXYBENZENE IN ALCOHOL (94 per cent.).

100 grams alcohol will dissolve at 0° 5.0 grams azoxybenzene.
100 grams alcohol will dissolve at 15° 11.4 grams azoxybenzene.

The solubility of azoxybenzene in hot ligroin is so great that when cooled to 0° the solution practically solidifies completely; for purposes of recrystallization it is best to make a saturated solution at the ordinary working temperature and then cool in ice.

II. THE ACTION OF SULPHURIC ACID UPON AZOXYBENZENE.

As mentioned above, Wallach found that hot, concentrated sulphuric acid isomerizes azoxybenzene to *p*-hydroxyazobenzene. Another product of this reaction he found in azobenzene. Wallach's work was confined to the identification of these two substances. In view of the great importance of properly understanding intramolecular rearrangements, I devoted much time to

a study of the mechanism of this reaction, varying the experimental conditions within wide limits.

No intermediate compounds between azoxybenzene and hydroxyazobenzene could be discovered. When azoxybenzene and sulphuric acid are mixed, a dark red solution is formed, with slight evolution of heat. If the mixture is poured into water, azoxybenzene is recovered quantitatively. If allowed to stand in the cold for varying periods of time, the rearrangement proceeds slowly, and is not complete even after a week. If warmed on the water-bath, the reaction proceeds with greater or less velocity, depending upon so many factors that it seems hopeless to find any relationship between them. But in all cases, much the same products are formed in varying amounts, and with more or less unchanged azoxybenzene if the process be interrupted before completion.

Besides the products obtained by Wallach, I have isolated three others. An almost constant product is a black, amorphous powder, insoluble in all ordinary solvents, infusible, difficult to wash, and evidently a high molecular polymerization-product not far removed from free carbon. It contains nitrogen, however. Another product of the reaction is *p*-hydroxyazobenzene-*p*-sulphonic acid. A third product, usually in very small amounts, is an amylamine, probably normal. Its formation is to be explained by an opening of one of the benzene rings in azoxybenzene, with simultaneous oxidation of a carbon atom. Besides these substances, traces of one or more reducing compounds, probably aminophenol and related substances, are usually present; I have not been able to isolate them. Finally, the formation of *o*-hydroxyazobenzene described by Bamberger[1] not long ago could be verified.

These products are formed in amounts depending upon the following factors: the initial temperature of the reaction, the maximum temperature, the concentration of the acid employed, the ratio of sulphuric acid to azoxybenzene, the duration of the experiment, and finally, upon the size and the shape of the containing vessel. The last factor, which may seem captious, finds its explanation in a hitherto unnoticed circumstance; for the reaction of sulphuric acid upon azoxybenzene is strongly exothermic, and may proceed with explosive violence. Ten grams of

[1] *Ber. d. chem. Ges.*, **33**, 3192 (1900).

each substance were warmed on the water-bath; after eleven minutes, the mixture shot out of the flask, with evolution of much sulphur dioxide and oxides of nitrogen, and the formation of voluminous carbon fully twenty times the capacity of the flask. At least three times as much acid as azoxybenzene must be taken to avoid this violent result, as a number of tests showed. Even then, the temperature of the liquid rises above 200°. It is clear that under these circumstances the temperature of the mixture is largely dependent upon the amount of radiation to the outside, which again is a function of the size and shape of the vessel, as well as of the absolute amounts of material taken.

Just what the influence of temperature upon the final result may be, my experiments have not sufficed to determine. As already mentioned, the reaction proceeds slowly even in the cold. On the other hand, I twice carefully warmed a mixture of 10 grams each of sulphuric acid and azoxybenzene (the explosive mixture above) to 85° for ten and for twenty minutes, and recovered 97 and 92 per cent. respectively of unchanged azoxybenzene. The larger the ratio of acid to azoxybenzene, the lower the temperature at which the reaction completes itself; using 200 grams of acid to 10 grams of substance, complete action was obtained at a temperature not exceeding 74°.

It is unnecessary to detail each one of the numerous tests I have made of this reaction; the general conditions that seem to determine the amount of each product will suffice. First a brief account of the method of separation. After warming the mixture for the desired time, it is poured into cold water. Azobenzene, both hydroxyazobenzenes, and the black powder separate. The mixture is shaken out with ether, whereby the powder causes troublesome emulsions; after each extraction, it is best to filter the ether through the same funnel, where the powder finally collects. After being thoroughly washed with ether, the powder must be washed with water to remove sulphuric acid (which it holds tenaciously), and then dried in air. The ether extract is shaken out with dilute alkali to remove hydroxyazobenzene, and then distilled; azobenzene remains, with whatever unchanged azoxybenzene may be recovered. These two substances must be separated by crystallization from alcohol. The alkaline solution

of hydroxyazobenzene is precipitated with an excess of mineral acid, and the compound filtered, washed and dried in air. The original aqueous acid solution contains the sulphonic acid of hydroxyazobenzene, and amylamine. It is rendered alkaline with caustic soda and distilled with steam; the amine passes over very quickly, is collected in hydrochloric acid, and obtained as a salt by evaporation on the water-bath. The residual alkaline solution rapidly darkens in air, and shows reducing action towards ammoniacal silver nitrate, etc. To separate the sulphonic acid, it is rendered slightly acid with sulphuric acid, and boiled down sufficiently to give a saturated solution of sodium sulphate on cooling. The sodium salt of hydroxyazobenzene sulphonic acid separates, being rather insoluble in cold water and still less in sodium sulphate solution.

A. p-Hydroxyazobenzene.—The best yields of hydroxyazobenzene are obtained by using a somewhat diluted sulphuric acid, about 85 per cent. (corresponding to $H_2SO_4 + H_2O$), by taking from five to twenty times as much acid as azoxybenzene, and by keeping the temperature low. From 60 to 75 per cent. of the azoxybenzene may be obtained in its isomeric form. Freed from the ortho-compound as indicated below, and recrystallized from alcohol, it may be obtained in a state of great purity. For the *preparation* of hydroxyazobenzene, the synthetic method of Griess (from diazobenzene and phenol) is much simpler and quicker, as well as less expensive.

B. o-Hydroxyazobenzene.—This compound was first isolated by Bamberger.[1] It is volatile with steam, and can be readily separated from the para compound. From 40 grams mixed *o*- and *p*-hydroxyazobenzene (obtained from 75 grams azoxybenzene in various experiments), I separated 1.5 grams bright red *o*-hydroxyazobenzene (m. p. 81° before recrystallizing). Bamberger registered 190° at the moment of violent action, but as the fluid of the above yield.

C. The Black Powder.—The amount of this amorphous product varies within wide limits—from a trace to 30 per cent. of the azoxybenzene taken. It is formed in greatest amount when the temperature is high and the ratio of acid to azoxybenzene low.

[1] *Loc. cit.*

There is no reason to believe that this substance has a uniform composition. Nothing definite could be learned about it, except that it is in some way related to the formation of amylamine during the rearrangement. Five grams of the powder were heated with 40 cc. concentrated sulphuric acid to 100° for three hours; 0.09 gram amylamine hydrochloride was obtained. In another test, 3.2 grams of powder were heated in a sealed tube with diluted sulphuric acid (1:1): time, three hours; temperature, 220°; yield, 0.35 gram. In a third test, 3 grams were heated almost to fusion with strong caustic soda solution, and the volatile bases collected; 0.30 gram impure salt, giving slight aniline reaction, was obtained.

It seems likely that the powder contains the amylamine group pre-formed, and that the base is detached from the rest of the complex by the action of various agents.

D. Amylamine.—During the first experiments, the amount of amylamine hydrochloride obtained varied from 0.5 to 7 per cent. of the azoxybenzene taken, without affording any clue as to the determining factor. The above experiments with the black powder, and the observation of the high temperature accompanying the rearrangement, suggested the dependence of this product upon the high temperature. A direct trial gave ample confirmation of this view.

Twenty grams azoxybenzene and 45 grams concentrated acid were allowed to heat on the water-bath. An inserted thermometer registered 190° at the moment of violent action, but as the fluid then completely covered the stem, further reading was impossible. Much of the mixture was lost by the explosion, but the collected residues yielded 2.7 grams hydrochloride, a yield of 14 per cent. on the total amount of azoxybenzene.

Amylamine hydrochloride, as obtained by this curious method, forms white needles. It is very soluble in water and in alcohol, but is not deliquescent. With chlorplatinic acid it forms a very insoluble, yellow, prismatic powder, which cannot be recrystallized from water, for it is decomposed, with the separation of metallic platinum, considerably below 100°. Heated in the ordinary melting-point apparatus, it sublimes above 150°; heated quickly on platinum, it can be made to melt, but rapidly volatilizes

under these conditions. It is the salt of a primary base, as shown by the intense isonitrile reaction. For analysis, the salt was recrystallized from water, and dried over sulphuric acid for a few hours.

Analysis:

I. 0.2061 gram gave 20.1 cc. moist nitrogen at 20° and 750 mm.

II. 0.2359 gram gave 0.2712 gram silver chloride.

	Calculated for $C_5H_{11}NH_2.HCl$.	Found.
Nitrogen	11.33	11.13
Chlorine	28.67	28.42
Atomic ratio N : Cl	1 : 1.006	

For lack of time, no experiments were made with the free base, except to note that its boiling-point is about 100°, and that it is quite soluble in water. At some subsequent date, an attempt will be made to study this base, and to work out this somewhat unusual method of preparation. Normal amylamine has been described only by Hofmann,[1] and was evidently obtained by him in very small amount. As prepared above, the base seems to be quite free from ammonia, as well as from secondary or tertiary bases.

E. Hydroxyazobenzene Sulphonic Acid.—The formation of this substance offers no difficulties of explanation; it is a simple case of sulphonation. This is usually a reaction with small velocity; and in this instance, the amount of sulphonic acid produced depends more upon the time during which the substances act upon each other than upon the ratio of acid to azoxybenzene. The maximum yield observed in my experiments was 11 per cent. of the sodium salt (of the weight of azoxybenzene taken). This yield can of course be greatly increased by prolonged heating. A more detailed study of this acid is given below.

F. Azobenzene.—During the energetic rearrangement of azoxybenzene, azobenzene is a constant product. It is formed in amounts varying from 30 to 60 per cent. of the original substance. Being formed in such large quantity, it was by no means clear that it is merely a by-product, as Wallach regarded it; and it was hoped that a careful study of the formation of azobenzene would greatly assist the explanation of how hydroxyazobenzene is formed.

[1] *Ber. d. chem Ges.*, 15, 770 (1882).

For it is evident that we have three possibilities involved: azobenzene is formed from hydroxyazobenzene; hydroxyazobenzene is formed from azobenzene; or finally, that both are formed simultaneously.

The last possibility, that both are formed at the same time, is ruled out by one experiment. 8.3 grams azoxybenzene stood in the cold for six days, with 35 grams of sulphuric acid of the strength $H_2SO_4 + H_2O$. The products of this reaction were 5.2 grams hydroxyazobenzene and 3 grams unchanged azoxybenzene; mere traces of amylamine and of the sulphonic acid were also observed.

A choice between the first two possibilities was afforded by a direct experiment in which 5 grams of pure hydroxyazobenzene were heated on the water-bath with 20 cc. sulphuric acid ($H_2SO_4 + H_2O$). The products were: Black powder, 0.05 gram; amylamine, unweighable trace of hydrochloride; unchanged hydroxyazobenzene, 3.85 grams; azobenzene, 0.70 gram; sulphonate, 0.45 gram.

It seems clear that the formation of azobenzene is the result of auto-reduction of hydroxyazobenzene; as oxygen is not given off, the black powder is to be regarded as the oxidation product. We have here a case similar to the auto-reduction and auto-oxidation of benzaldehyde under the influence of caustic potash,

$$2\,C_6H_5CHO = C_6H_5CH_2OH + C_6H_5COOH,$$

except that for hydroxyazobenzene the reaction is n-molecular rather than bi-molecular,

$$n\,C_6H_5N{=}NC_6H_4OH = (n{-}x)C_6H_5N{=}NC_6H_5 + [x\,C_6H_5N{=}NC_6H_4OH.(n{-}x)O],$$

where n is a large number, and x a small one.

G. The Mechanism of the Rearrangement.—Further efforts to isolate intermediate products in the rearrangement of azoxybenzene proved futile. Adding acetic anhydride to the sulphuric acid gave results practically the same as above; the products were azo- and hydroxyazobenzene, and the black powder, the amine and the sulphonate being formed only in traces. The direct action of acetic anhydride was also tried; on heating azoxybenzene with it to 200° for five hours, a trace of hydroxyazobenzene was obtained,

but the bulk of azoxybenzene was recovered unchanged (4.8 grams from 5 grams).

A number of explanations have been offered for this rearrangement. Wallach and Belli[1] assume that the first products are phenol, diazobenzene sulphonic acid, and oxygen; and that the former then couple, eliminating sulphuric acid. The oxygen is not accounted for. Friswell and Green[2] similarly assume diazobenzene and phenol as the primary products, which then couple. Other, equally hypothetical explanations are quoted by Beilstein.[3] As I have found hydroxyazobenzene to be formed at temperatures much exceeding 100°, the assumption of a normal diazo reaction in hot sulphuric acid seems somewhat forced. If phenol were formed, its ready sulphonation would lead one to expect at least a small amount of some phenolsulphonic acid in the final product, but such is not the case.

I am inclined to regard the formation of hydroxyazobenzene in this reaction as a direct and immediate intramolecular rearrangement, as are so many other rearrangements of aromatic nitrogen compounds; there is no valid reason for assuming diazobenzene as intermediate. The other products of the reaction, as has been shown above, are secondary in their nature, and can all be obtained from pure hydroxyazobenzene.

It is interesting to note that Zinin, the discoverer of azoxybenzene,[4] tried the action of concentrated sulphuric acid upon this substance, but obtained only unchanged azoxybenzene together with some "gepaarte Schwefelsäureverbindung".

III. *p*-HYDROXYAZOBENZENE-*p*-SULPHONIC ACID.

The sulphonic acid obtained by the action of sulphuric acid upon azoxybenzene was subjected to closer examination, owing to certain discrepancies in the literature. By direct synthesis,[5] the action of diazobenzene-*p*-sulphonic acid upon phenol gives *p*-hydroxyazobenzene-*p*-sulphonic acid,

$$HO_3S—C_6H_4N=N—OH + C_6H_5OH = HO_3S—C_6H_4N=NC_6H_4OH + H_2O.$$

[1] *Ber. d. chem. Ges.*, 13, 525 (1880).
[2] *J. Chem. Soc.* (London), 47, 923 (1885).
[3] Third Edition, Vol. IV, p. 1407.
[4] *Loc. cit.*
[5] Griess: *Ber. d. chem. Ges.*, 11, 2192 (1878).

On the other hand, Wilsing[1] has described a sulphonic acid of the same constitution, but with different properties, which he obtained by the action of sulphuric acid upon azoxybenzene. In undertaking this work, Wilsing was guided by Wallach's recent discovery of the rearrangement to hydroxyazobenzene.

Wilsing's method of preparing his sulphonic acid was to heat azoxybenzene with fuming sulphuric acid (strength not given) to 110° for several hours, until a product completely soluble in water was obtained. In this way, he isolated not only a monosulphonic acid, but also a di-, tri-, and tetra-sulphonic acid. Wilsing himself carefully compared his own mono-sulphonic acid with the synthetic substance, and found many notable points of difference. The most striking difference was met in the action of bromine water; the synthetic product gave a precipitate of tribromphenol, whereas Wilsing's acid was indifferent even at 100°.

On the other hand, the sulphonic acid which I obtained above reacted readily with bromine water as indicated, and was found to be identical in every respect with the synthetic acid. Wilsing's acid cannot possibly have the constitution he assigned to it. In all probability he had azobenzene-sulphonic acid, for the conditions under which he worked (highly concentrated acid) are those which I have found to give chiefly azobenzene as the main product of the rearrangement. The discrepancies in Wilsing's analyses are easily accounted for by the fact that he analyzed the *anhydrous salts* of the acid. I have found the anhydrous salts of these sulphonic acids to be extremely hygroscopic; it is almost impossible to completely dehydrate them by ordinary methods, and the dehydrated salts will gain in weight even in a calcium chloride desiccator; an azobenzene sulphonate containing 1 molecule of water will, of course, give the same analytical results as an anhydrous hydroxyazobenzene sulphonate.

During this comparison I became interested in the manner in which tribromphenol is formed from hydroxyazobenzene sulphonic acid. I used the sodium salt, which was first prepared by Limpricht;[2] it contains 2 molecules of water:

0.7072 gram lost 0.0722 gram at 160°-170°.

[1] *Ann. Chem.* (Liebig), **218**, 228 (1882).
[2] *Ibid.*, **263**, 239 (1890).

	Calculated for $Na.C_{12}H_8N_2SO_4 + 2H_2O$.	Found.
Water	10.7	10.2

The salt requires 140 parts of water at 15° for solution, and crystallizes from hot water in golden yellow, glistening plates of very small size. The anhydrous salt is extremely hygroscopic; two samples, kept in separate calcium chloride desiccators over night, had each gained more than 5 mg.

The sodium sulphonate obtained from azoxybenzene had the same composition, and showed the same solubility.

0.5708 gram lost 0.0574 gram.

	Calculated.	Found.
Water	10.7	10.1

A. The Action of Bromine Water on Hydroxyazobenzene Sulphonic Acid.—When bromine water is added to a solution of this acid (or its sodium salt), a precipitate of tribromphenol is formed instantly. Exactly 6 atoms of bromine are taken up by 1 molecule of the salt. 1.06 grams synthetic sodium salt were titrated with standard bromine water (0.1918 N). When 99.1 cc. had been added, the solution was colorless, and did not smell of bromine; addition of 0.5 cc. bromine water caused a pronounced odor of bromine, which lasted after ten minutes' shaking. One molecule of salt required 6.02 atoms of bromine.

The tribromphenol was filtered and washed: Found, 1.01 grams; calculated, 1.04 grams. The filtrate on evaporation gave the sodium salt of phenolsulphonic acid. (Weighed after drying at 112°). Found, 0.65 gram; calculated, 0.62 gram.

An exactly similar result was obtained with the sulphonate obtained from azoxybenzene: 0.47 gram sodium salt gave 0.48 gram tribromphenol; calculated, 0.47 gram. The filtrate gave 0.29 gram sodium phenolsulphonate; calculated, 0.28 gram.

Finally, the free synthetic sulphonic acid was similarly treated, to make sure that the reaction was not confined to its salts. 0.50 gram sulphonic acid gave 0.56 gram tribromphenol; calculated, 0.59 gram.

The formation of phenolsulphonic acid during this reaction seemed mysterious at first; it was then found to be a secondary product, derived from an *intermediate diazo compound*. The solution, after the addition of bromine water, gives up exactly 1

molecule of diazo nitrogen when boiled (atmosphere of carbon dioxide).

Diazo nitrogen: 0.4579 gram synthetic sodium salt gave 30.7 cc. nitrogen at 13.5° and 741 mm.

	Calculated.	Found.
Nitrogen	8.3	7.8

The diazo compound obtained here belongs to the normal, and not to the iso series. In two separate tests, the filtrate from the precipitated tribromphenol was run into alkaline β-naphthol, within less than twenty seconds from the first addition of bromine. In each case, immediate formation of an azo dye was noticed. The solution therefore contained normal diazonium-bromide-*p*-sulphonic acid.

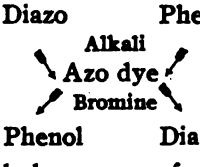
The above analyses permit of a very accurate formulation of the action of bromine upon oxyazobenzene sulphonic acid. The first products are tribromphenol and the diazo compound:

$$HO_3S—C_6H_4N=NC_6H_4OH + 6Br = C_6H_2Br_3OH + HO_3S—C_6H_4N_2Br + 2HBr.$$

The second step consists in the hydrolysis of the diazonium salt:

$$HO_3S—C_6H_4N_2Br + H_2O = HO_3S—C_6H_4OH + N_2 + HBr.$$

These results are of interest from two points of view. In the first place, we have a reversal of the ordinary coupling reaction of diazo compounds. These react with phenols (in alkaline solution) to form azo dyes; here an azo dye (in acid solution) breaks down into a phenol and a diazo compound:



We have all the typical phenomena of a reversible reaction. This is all the more curious since we usually contrast the stability of azo compounds with the instability of diazo compounds; compare Meyer and Jacobson[1]: "Zünachst ist die grosse Beständigkeit (der Azoverbindungen) hervorzuheben, die im denkbar grössten Gegensatz zu der Unbeständigkeit der Diazoverbindungen steht".

[1] "Lehrbuch," Vol. II, p. 254.

An entirely similar result, for which the explanation is now at hand, was obtained by Witt,[1] who found that chrysoidine (diaminoazobenzene) gives phenol and nitrogen when heated to 150° with dilute hydrochloric acid.

In the second place, the above facts have some bearing upon the theories of Armstrong[2] and of Hewitt.[3] These investigators hold that hydroxyazo compounds possess two *isodynamic* (tautomeric) structures: in alkaline, or it may be neutral solution, or in any medium which fixes the hydroxyl group as such (*e. g.*, glacial acetic acid), we have true hydroxyazo compounds (as formulated above). In acid solution, however, the presence of derivatives of quinonephenylhydrazone is indicated; *e. g.*,

$$HO_3S—C_6H_4NH—N=C_6H_4=O.$$

These authors have attacked the problem experimentally by studying the bromination of the oxygenated benzene ring; a para-substituted phenol is usually brominated in positions 2 and 6; quinone, on the other hand, would *add* bromine first in positions 2 and 3, then in 5 and 6. Thus Hewitt found that hydroxyazobenzene with bromine water gives di-*o*-bromhydroxyazobenzene, and concludes that it is a true hydroxy compound.

The same appears to be true to the hydroxyazobenzene sulphonic acid studied above, in spite of the much greater acidity of its solutions; for it also furnishes a di-*o*-substituted phenol. Another consideration leads to the same result. If we imagine tribromphenol formed from the tautomeric structure given above, the hydrazone molecule would form *iso*-diazobenzene-*p*-sulphonic acid,

$$HO_3S—C_6H_4NH—N=C_6H_4=O \rightarrow HO_3S—C_6H_4NH—NO,$$

whereas we really have a normal diazonium salt produced. We may conclude that there is no reason for assigning to hydroxyazobenzene-*p*-sulphonic acid any other structure than the one indicated by its name.

IV. MISCELLANEOUS REACTIONS OF AZOXYBENZENE.

A. The Action of Hydrochloric Acid upon Azoxybenzene.—Azoxybenzene is quite indifferent towards hydrochloric acid.

[1] *Ber. d. chem. Ges.*, 10, 656 (1877).
[2] *Proc. Chem. Soc.*, 15, 243 (1899); 16, 158 (1900).
[3] *J. Chem. Soc.* (London), 77, 810 (1900).

Upon heating 1 gram in a current of the dry gas to 100° for two hours, considerable gas seemed to be absorbed; but this escaped on brief exposure to the air, and the azoxybenzene was unchanged in weight and in melting-point.

Similar negative results were obtained upon heating azoxybenzene with concentrated hydrochloric acid solution (sp. gr. 1.20); four hours at 175° produced no change, nor did five hours at 200°. On heating another sample for eight hours to 225°, the azoxybenzene was completely changed, the tube contents were black, much tar was formed, some gas, and the solution gave reactions for phenol, aminophenol, and chlorinated aniline. No hydroxyazobenzene was obtainable. The reaction was not examined further. Werigo[1] has studied the action of hydrobromic acid upon azoxybenzene, and isolated only dibromaniline. From the action of hydriodic acid upon azoxybenzene he obtained some benzidine.

B. The Action of Hydroxylamine upon Azoxybenzene.—Four grams azoxybenzene were boiled with free hydroxylamine and a great excess of potash in methyl alcohol. After six hours, the mixture yielded 3.8 grams unchanged azoxybenzene, and traces of aniline and of azobenzene. Ten grams azoxybenzene were similarly heated in a pressure flask to 100° for sixteen hours. The mixture yielded 8.1 grams azobenzene (90 per cent. of theory), traces of aniline, 0.01 gram *o*-hydroxyazobenzene (m. p. 80°), and 0.02 gram *p*-hydroxyazobenzene (m. p. 150°).

From these experiments it is clear that the action of hydroxylamine upon azoxybenzene is very slow, and consists almost wholly of simple reduction. The formation of the isomeric hydroxyazobenzenes under these conditions is very interesting; but the amounts are very small.

C. The Action of Phenylhydrazine upon Azoxybenzene.—Ten grams azoxybenzene and 5 grams phenylhydrazine were heated to 110° for four hours. Aside from a slight evolution of ammonia, no action could be observed; and all of the azoxybenzene was recovered unaltered.

D. The Action of Zinc Ethyl upon Azoxybenzene.—Two grams azoxybenzene were allowed to stand with 4 grams of zinc ethyl for sixteen days; no action was observable, and all of the azoxyben-

[1] *Ann. Chem.* (Liebig), 168, 202 (1872).

zene (1.9 grams) was recovered. On heating azoxybenzene with zinc ethyl, a very complex reaction took place. 11.3 grams azoxybenzene were boiled with an excess of zinc ethyl (18 grams) in benzene solution. After one hour, 1000 cc. of gas had been evolved; in another hour, 100 cc. more were collected. This gas contained 27 per cent. ethylene; the balance consisted of ethane. On pouring into dilute sulphuric acid, a basic and a neutral oil were obtained. The basic oil (8 grams) contained aniline and ethyl aniline, and much tar; diethylaniline was carefully sought for, but not found. The neutral oil was directly distilled, and seemed to be thoroughly decomposed during this process. The liquid portion of the distillate seemed to be composed of about equal parts of aniline and ethylaniline. Here again diethylaniline was looked for,[1] but could not be detected. During the distillation, a combustible, basic gas was liberated, probably ethylamine.

No rational equation can be given for the action of zinc ethyl on azoxybenzene. A complex reduction occurs, and the nitrogen atoms seem to be separated. It is possible that in the neutral oil some intermediate product exists, but no suitable method for separating it could be found. This reaction will be the subject of renewed investigation later on.

V. SOME REACTIONS OF DIPHENYLNITROSAMINE.

For reasons to be given further on, it was necessary to subject diphenylnitrosamine to the same reagents used with azoxybenzene. In almost every instance, diphenylnitrosamine gave positive and decisive results under conditions where azoxybenzene gave negative or undecisive ones.

The action of zinc ethyl upon diphenylnitrosamine has already been carefully studied.[2] It will suffice here to summarize the results. When the two substances are brought together, an addition product is formed with almost explosive violence. This addition product, when treated with water, breaks down quantitatively into diphenylamine, diethylhydroxylamine, and zinc hydroxide.

[1] The method of separation employed in this experiment consisted in the use of nitrous acid. The oil was treated with hydrochloric acid and sodium nitrite, after first adding ice and ether. The ethylaniline was immediately extracted as nitrosamine. The residual solution was halved; one part was precipitated with alkaline naphthol, and the azo dye weighed. The other part was distilled with dilute alkali, but gave no diethylamine (from possible nitrosodiethylaniline).

[2] Lachman: *Am. Chem. J.*, 21, 433 (1899); *Ber. d. chem. Ges.*, 33, 1022 (1900).

A. The Action of Hydrochloric Acid.—When dry hydrochloric acid gas is allowed to act upon diphenylnitrosamine, even at 0°, nitrosyl chloride is split off. The substance can be readily recognized by its characteristic properties, and when led into potassium iodide solution it liberates iodine and nitric oxide. A quantitative experiment showed that the whole of the nitroso group in diphenylnitrosamine is thus eliminated: 1 gram diphenylnitrosamine (dissolved in ligroin) was treated at 0° with hydrochloric acid gas, and the evolved gases conducted into potassium iodide. Air was carefully excluded by carbon dioxide, as otherwise much iodine is liberated by the catalytic action of nitric oxide. The iodine was titrated with sodium thiosulphate, after first driving out all nitric oxide.

	Calculated	Found.
Iodine	0.641	0.622

The action[1] is represented by the following equation:

$$(C_6H_5)_2N.NO + HCl = (C_6H_5)_2N.H + NOCl.$$

The diphenylamine left after the reaction is not pure, apparently owing to the formation of polymeric products.

B. The Action of Hydroxylamine on Diphenylnitrosamine.—Hydroxylamine and diphenylnitrosamine react in alkaline solution to form diphenylamine and nitrous oxide. Both of these products were obtained quantitatively. Four grams diphenylnitrosamine, 2 grams hydroxylamine hydrochloride, and an excess of methyl alcoholic potash were boiled until the evolution of gas ceased. The gas consisted of nitrous oxide (see below) and contained traces of nitric oxide, as shown by potassium iodide paper. The residual solution was evaporated and extracted with ether and then gave 3.4 grams pure diphenylamine (calculated 3.4 grams). No unchanged nitrosamine was left, for the diphenylamine solution. A direct test showed that less than 0.1 per cent. of nitrosamine in diphenylamine gave a deep blue color under these conditions. One gram nitrosamine was boiled with a slight excess of free hydroxylamine in an atmosphere of carbon dioxide (methyl alcohol solution). 113 cc. moist nitrous oxide were obtained (16° and 737 mm).

[1] See the explanation of this reaction which I have given: *Ber. d. chem. Ges.*, 33, 1038 (1900).

	Calculated.	Found.
Nitrogen.....	0.22	0.20

In all probability, the first action of hydroxylamine on diphenylnitrosamine results in a normal, oxime-like condensation,

$$(C_6H_5)_2N.NO + H_2NOH = (C_6H_5)_2N.N{=}NOH + H_2O.$$

The intermediate product is unstable (it could not be isolated), and breaks down into nitrous oxide and diphenylamine,

$$(C_6H_5)_2N.N{=}NOH = (C_6H_5)_2NH + N_2O.$$

The reaction proceeds rapidly in the presence of free alkali, requiring not more than fifteen minutes; in the absence of alkali it takes about an hour.

C. The Action of Phenylhydrazine on Diphenylnitrosamine.—When molecular quantities of phenylhydrazine and diphenylnitrosamine are warmed on the water-bath, a violent reaction sets up. Much gas is liberated, and the mixture is shot out of the containing vessel. For the purpose of studying the reaction a little more carefully, two procedures were adopted. The first method consisted in carrying out the operation in sealed tubes. Four grams nitrosamine and 2.2 grams of phenylhydrazine were heated in an evacuated tube. After cooling, 420 cc. gas (corrected) were obtained. This gas was pure nitrogen; its weight is 0.53 gram (calculated for 1 molecule of nitrogen, 0.56 gram). The tube contents gave 3.2 grams diphenylamine, and a little aniline, the amount of the latter being too small to determine. No other products could be found in this or in several other similar experiments; benzene was carefully sought for, but no certain indication of its presence could be obtained.

The second method consisted in boiling the two substances in dry ether for from four to twelve hours. The gas given off under these circumstances contains considerable nitric oxide; if air has access to the flask, a little nitric acid[1] also forms. Nitric oxide also appears in small amount when the substances are heated in a sealed tube still containing air. Here again, no tangible product except diphenylamine could be isolated. From the same quantities as above 3.3 grams diphenylamine were found; calculated 3.4 grams.

[1] This was precipitated during the reaction as phenylhydrazine nitrate, which was analyzed. (Nitrogen found, 24.4 per cent.; calculated, 24.6.)

So far as the two products actually obtained are concerned, the equation may be written as follows:

$$C_6H_5NH—NH_2 + (C_6H_5)_2N.NO = (C_6H_5)_2NH + N_2 + ?(C_6H_5N).$$

It seems, however, that as an actual fact less phenylhydrazine is used up than is called for by this equation; about one-fifth can be recovered as benzalphenylhydrazone after adding benzaldehyde. This interesting reaction will be studied more closely hereafter. In some respects it closely resembles the action of phenylhydrazine on aromatic C-nitroso compounds, recently investigated by Clauser[1]:

$$R—NO + C_6H_5NHNH_2 = R—N< + C_6H_6 + H_2O + N_2.$$

Reference should also be made here to the action of hydrazine (diamide)[2] on diphenylnitrosamine; reduction occurs, diphenylamine and asym.-diphenylhydrazine being the products.

VI. THE CONSTITUTION OF AZOXYBENZENE.

The structure usually assigned to azoxybenzene,

$$C_6H_5—N(\rightarrow O)—N—C_6H_5, \qquad (I)$$

rests upon no direct evidence whatever, and within the last few years a number of authors[3] have suggested the following constitution as an alternative:

$$C_6H_5—N=N(=O)—C_6H_5. \qquad (II)$$

It must be said that as little direct evidence exists for this second structure as for the first. Brühl, to be sure, has found the refractive power of azoxybenzene to be greater than can be accounted for by (I), and even proposes a third structure as equally satisfactory to him:

$$C_6H_5—N\equiv N(\rightarrow O)—C_6H_5. \qquad (III)$$

[1] *Ber. d. chem. Ges.*, 34, 889 (1901). My own experiments were completed some months before Clauser's paper appeared.

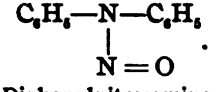
[2] Cited in Beilstein, third edition, Vol. II, p. 339. I was unable to find the author and the journal reference.

[3] Meyer-Jacobson: "Lehrbuch," Vol. II, p. 251 (1894); Bamberger: *Ber. d. chem. Ges.* 29, 2413 (1896); Brühl: *Ibid.*, 31, 1361 (1898); 33, 122 (1900).

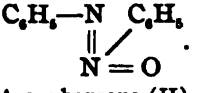
I confess my inability to see any valid differences between (III) and (I); and the present discussion will be confined to formulas (I) and (II). Nor will Brühl's "spectro-chemical" data be considered at this time, for extrapolations of this sort weigh little as *evidence* when applied to wholly unknown atomic groupings.[1]

The general indifference of azoxybenzene to reagents renders it almost impossible to deduce its structure from its own reactions, and for the purposes of the present investigation, a comparative method was chosen. This consisted in the study of the behavior of diphenylnitrosamine towards the same reagents.

There is a very close resemblance between the structure of diphenylnitrosamine and formula (II) above, which is clearly shown by a slightly different method of writing:



Diphenylnitrosamine.



Azoxybenzene (II).

In the first place, the two substances are isomeric; in the second place, each contains two phenyl groups; in the third place, each possesses two nitrogen atoms which are directly joined. Surely, if the similarity extends to the nitrogen-oxygen linking also, some slight similarity of behavior may be looked for in these two compounds.

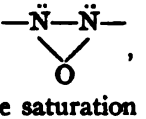
Upon comparing the results reached above, however, we find that no similarity whatever exists. At 0°, diphenylnitrosamine decomposes hydrochloric acid; at 200°, azoxybenzene is unable to do so. At the boiling-point of methyl alcohol, the nitrosamine reacts promptly with hydroxylamine; azoxybenzene is indifferent to it, and is but slowly reduced to azobenzene at a much higher temperature. Diphenylnitrosamine reacts violently with phenylhydrazine; azoxybenzene does not react at all. Diphenylnitrosamine adds zinc ethyl with great energy in the cold; azoxybenzene, on the other hand, does not act at all in the cold, and undergoes complex decomposition when heated with this reagent. Showing no similarity in its reactions to diphenylnitrosamine, azoxybenzene cannot have a similar structure; and nothing remains but to regard the older formula (I) as

[1] See Hantzsch, *Ber. d. chem. Ges.*, 32, 3148 (1899), for a similar opinion of the applicability of Brühl's data to nitrogen compounds.

the best expression of its chemical behavior; for, after all, the structural formula of a substance is but a condensed account of its chemical behavior.

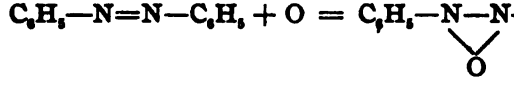
Another line of reasoning also leads to the exclusion of formula (II). Azobenzene, $C_6H_5 - N = N - C_6H_5$, which contains the doubly linked nitrogen atoms assumed in that structure, reacts[1] with zinc ethyl with great violence, yielding ethylene and aniline, (the latter in almost theoretical amount). If azobenzene on the one hand, and diphenylnitrosamine on the other, react so quickly and smoothly with zinc ethyl, the indifference of azoxybenzene points to a marked diversity of structure.

A knowledge of the true structure of azoxybenzene is important from one general point of view: this substance represents the most stable known form of union between oxygen and nitrogen in organic compounds. The azoxy grouping we have just seen to be more inert than the nitroso group; it is more inert than the nitro group. The amine oxides are also much more active than azoxy compounds. If this inertness means anything at all, it indicates that in the grouping,



we have the most complete saturation of the affinities of oxygen and nitrogen for each other.

This is well shown by thermochemical data; azobenzene may be directly oxidized[2] to azobenzene, and the reaction is accompanied by the evolution of considerable heat[3]:



Contrast this with the negative heat of formation of the oxides of nitrogen; for example: nitrous oxide, $2N + O = N_2O - 180K$; nitric oxide, $N + O = NO - 216K$; $N + 2O = NO_2 - 77K$.

Having thus definitely established the constitution of azoxybenzene, it will perhaps be justifiable to draw the general conclu-

[1] Frankland and Louis: *J. Chem. Soc.* (London), 37, 560 (1880).

[2] Petriew: Beilstein, Vol. IV, p. 1348. See also the easy oxidation of dinitroazobenzene to the azoxy compound; Werner and Stiasny: *Ber. d. chem. Ges.*, 32, 3263 (1899).

[3] Petit: *Ann. chim. phys.*, (6), 18, 160 (1889).

sion that in its nitrogen compounds a bridged oxygen atom shows little tendency towards chemical action, and to apply this conclusion to the study of the valence-problem in other nitrogen-oxygen compounds.

SAN FRANCISCO, August, 1902.

DERIVATIVES OF PHENYLETHER. III.

BY ALFRED N. COOK AND CHARLES F. EBERLY.

Received September 3, 1902.

IN papers[1] previously published, accounts were given of the preparation of several derivatives of phenylether by the action of orthobromnitrobenzene upon ortho-, meta-, and paracresolates of potassium, and by reducing, oxidizing, and sulphonating the resulting compounds. During the past few months the work has been continued and extended to the reaction between the cresols and parabromnitrobenzene with results as given in this paper and two others that will follow.

4-NITRO-2'-METHYL PHENYLETHER, $NO_2.C_6H_4—O—C_6H_4.CH_3$.

This compound was prepared by the action of parabromnitrobenzene upon potassium paracresolate (prepared by a method described in a previous article).[2] The reaction is represented by the following equation:

$$NO_2.C_6H_4Br + KO.C_6H_4.CH_3 = NO_2.C_6H_4OC_6H_4.CH_3 + KBr.$$

Molecular equivalents of the two reacting substances were heated in an oil-bath to 135° C. An action began, as was shown by the agitation of the fused mass, which continued for some time as long as heat was applied. When it was ended the temperature was raised to 160° without inducing any further action. There remained a dark brown liquid and a copious precipitate of potassium bromide. The yield was very good.

The nitro methyl phenylether was separated from the parabromnitrobenzene not acted upon, and other constituents, by fractional distillation under diminished pressure. In a good vacuum it boils about 60° higher than parabromnitrobenzene and much higher than the other contaminating substances.

[1] *Am. Chem. J.*, 24, 525-529; This Journal, 23, 806-813.

[2] This Journal, 23, 806.

4-Nitro-2'-methyl phenylether is a tasteless, oily, reddish brown liquid which is soluble in organic solvents in general. It did not solidify when subjected to a temperature considerably below zero. An attempt to oxidize the side-chain with chromic acid in acetic acid solution was unsuccessful. The phenylether was entirely destroyed. Under a pressure of 27 mm. it boils at 220°-222°. Two analyses for nitrogen gave 6.36 and 6.45 per cent.. Theory requires 6.11 per cent.

4-NITRO-2'-METHYL PHENYLETHER SULPHONIC ACID, $NO_2.CH_3.C_{12}H_7O.SO_3H$.

This compound was prepared by dissolving the corresponding ether in a small quantity of concentrated sulphuric acid by the aid of the heat of the boiling water-bath. The solution was then diluted with several volumes of water, the excess of sulphuric acid precipitated with lead chloride, and the excess of lead precipitated with hydrogen sulphide. On concentrating the solution to a small bulk a thick, syrupy, red liquid separated out. On redissolving in hot water and allowing to stand, however, it crystallized out in tufts of white needle-like crystals. After recrystallizing several times it melted sharply at 115°. It is soluble in acids, alcohol, and hot benzene, has a bitter taste, and the syrupy liquid previously mentioned has a sharp piercing odor. It also dyes the hands and cloth yellow while the crystalline substance does not do so. A weak, water solution of the acid did not give a precipitate with any of the metals. Its composition was determined by the analysis of the barium salt given below.

Barium Salt, $(CH_3.NO_2.C_{12}H_7O.SO_3)_2Ba$.—This salt was prepared by adding sufficient barium chloride to the diluted sulphuric acid solution of the ether to remove all of the sulphuric acid and change all of the free sulphonic acid to the barium salt. It is one of the least soluble salts that have been prepared, on account of which most of it was precipitated with the barium sulphate and had to be extracted from it with hot water, from which it crystallized out in yellow crystalline grains, on cooling. 13.27 parts of the salt are soluble in 1000 parts of hot water at the temperature of the boiling water-bath, and 3.77 parts are soluble in 1000 parts of water at 24° C.

It is therefore approximately twice as soluble as the correspond-

ing salt of 2-nitro-2'-methyl phenylether and about half as soluble as the corresponding strontium salt. Two determinations of the barium after purification by recrystallization from water gave 18.38 and 17.89 per cent. barium. Calculated for $(C_{13}H_{10}O_6NS)_2Ba$, 18.18 per cent.

Copper Salt, $(NO_2.CH_3.C_{12}H_7.SO_3)_2Cu + 5?H_2O$.—The copper salt was prepared by treating a water solution of the barium salt with a molecular equivalent of copper sulphate in water. On concentrating the filtrate a greenish yellow powder was obtained which was desiccated over sulphuric acid. On being heated in the air-bath for some time at 100° it lost in weight and turned brown. On being allowed to come in contact with the air for a few hours it increased in weight and assumed its original color. The results of the determination of the water of crystallization were only fairly satisfactory, but corresponded nearest with 5 molecules.

The Sodium Salt was prepared by treating a water solution of the barium salt with a molecular equivalent of sodium carbonate in water. It crystallized as a fine yellow powder which melted at 233°. It is very soluble in water and the solution is much more yellow than the salt itself.

The Potassium Salt, prepared in an analogous manner with the sodium salt, crystallized from a concentrated water solution in small, yellow flakes which melted at 205°.

4-AMINO-2'-METHYL PHENYLETHER, $CH_3.C_6H_4OC_6H_4.NH_2$.

The free amino compound was prepared from the amino hydrochloride described below by precipitation with ammonium hydroxide. It is soluble in alcohol and benzene, insoluble in ether, and melts at about 60°. Its composition was determined by the analysis of the hydrochloride.

The Amino Hydrochloride was prepared by reducing 4-nitro-2'-methyl phenylether with tin and hydrochloric acid in alcoholic solution while warming on the water-bath. The tin was precipitated with hydrogen sulphide and the filtrate concentrated to crystallization on the water-bath when it assumed a pink tint. It crystallized in long needles and scales, but was recrystallized with difficulty, owing to decomposition. It melted at 182°-183°, and is soluble in alcohol, but insoluble in benzene and ether. Two

analyses of the hydrochloride for chlorine gave 15.15 and 14.88 per cent. Calculated, 15.08 per cent.

The Nitrate was prepared by dissolving the free amino derivative in dilute nitric acid. On cooling, it crystallized in flaky crystals which melted with decomposition at 153°-155°. It is soluble in alcohol and water, but insoluble in organic solvents in general.

The Sulphate, prepared in the same manner as the nitrate, separates from a water solution on cooling in warty crystals. It melts with decomposition at 155°-160°.

The Hydrobromide, prepared in an analogous manner with the two preceding, is soluble in water and alcohol, but insoluble in organic solvents in general. It crystallizes from a water solution in warty aggregations like the sulphate, and melts with decomposition at 200°-204°.

The Platinum Salt was prepared by precipitation from a water solution of the hydrochloride with a solution of chlorplatinic acid. It is a light brown substance which melts with decomposition at 180°-190°. A specimen which had been desiccated over sulphuric acid, when heated in the air-bath at 100°, lost in weight, but increased to its original weight when allowed to remain in contact with the air for some time. Our substance was not of sufficient purity, on account of the difficulty of purifying the hydrochloride from which it was made, to determine the number of molecules of water of crystallization with a high degree of accuracy, but it is probably one.

DINITRO METHYL PHENYLETHER, $(NO_2)_2.CH_3.C_{12}H_7O$.

In the first article on the "*Derivatives of Phenylether*" attention was called to the fact that nitric acid acted on the nitro-methyl derivatives of phenylether, but until the present no attempt was made to study the reaction. On simply mixing the two substances the temperature was slightly raised and the nitric acid assumed a reddish color. On warming, a violent action set in with the evolution of dense brown fumes, the temperature rose to 90°, and the phenylether passed completely into solution. Continued application of heat did not, apparently, cause any further action. The resulting solution was of a deep red color. On diluting with water there was precipitated a yellow oil. On repeated washing

with water and kneading with a glass rod it became viscous and finally solidified, and after repeated crystallization from hot alcohol it melted at 125°.

Nitro-4-nitro-2'-methyl phenylether is a yellow crystalline substance which is soluble in sulphuric ether, petroleum ether, benzene, nitrobenzene and aniline. An attempt to obtain an amino derivative by reducing with tin and hydrochloric acid was unsuccessful, owing to its decomposing when an attempt was made to evaporate the solution to crystallization. The results of the analysis for nitrogen together with its mode of formation, would lead us to the conclusion that it is a dinitro methyl phenylether. Two analyses for nitrogen gave 10.55 and 10.35 per cent. Calculated, 10.22 per cent.

MORNINGSIDE COLLEGE,
SIOUX CITY, IOWA.
August 10, 1902.

THE DETERMINATION OF MANGANESE IN IRON AND STEEL.

BY JOHN V. R. STEHMAN.
Received September 13, 1902.

WALTERS,[1] has shown that ammonium persulphate in the presence of a small amount of silver nitrate can be employed to advantage in place of lead peroxide, for the oxidation of manganese in the colorimetric method.

The writer has been using lead peroxide as an oxidizing agent and titrating the permanganic acid, with a standard solution of sodium arsenite after first filtering free from lead oxides, through an asbestos filter.[2]

In attempting to replace the lead peroxide by the ammonium salt and titrating as before, the silver salt, of course, caused trouble. If, however, the silver salt is thrown out of solution before titration is begun, as insoluble silver chloride, the determination of the permanganic acid by a standard solution of sodium arsenite may be readily accomplished.

The silver salt can be precipitated by a solution of sodium chlo-

[1] *Age of Steel*, November, 1901; This Journal, 24, R. 12.
[2] Blair's "Analysis of Iron," third edition.

ride, giving to the solution a fine white background, in which the end-reaction is well marked. It was found necessary with pig irons, to filter free from graphite after solution, as the graphite gives to the solution a peculiar color, in which it was difficult to distinguish the end-reaction.

The following is the method adopted: Weigh off into a 6-inch test-tube 0.2 gram of the sample; add 10 cc. nitric acid (sp. gr. 1.20), heat to boiling in hot water-bath till dissolved, and free from nitrous fumes. Filter into a 10 by 1-inch test-tube (using a small filter), wash filter twice with hot water containing a little nitric acid, and add through the filter to the contents of tube, 15 cc. of a solution of silver nitrate (1.33 grams to the liter). One gram of ammonium persulphate is now added and the solution brought to the boiling-point, using a free flame; heating is continued for about one minute after oxidation begins. The tube and contents are now cooled rapidly under the spigot and poured into a No. 2 beaker, washing out the tube with 30 or 40 cc. of water; 5 cc. of a saturated solution of sodium chloride are now added to the solution in the beaker, silver chloride being precipitated immediately, and titration is begun at once with standard sodium arsenite. The sodium arsenite solution is standardized against standard permanganate or it may be standardized by an iron in which the manganese has been accurately determined. The former is the more rapid and will be found to check closely with the latter.

The ammonium persulphate, as pointed out by Walters,[1] causes complete oxidation only when damp; he therefore adds 10 cc. of water to each pound of the salt the day before used. A determination by the above method may be made in twenty-five minutes in the case of pig irons; with steels, where filtration is not necessary and the sample can be dissolved directly in a large test-tube, the method is more rapid than the color method in which lead peroxide is used as an oxidant.

Below are a few results obtained in pig irons.

[1] *Loc. cit.*

Mn present. Per cent.	Mn found. Per cent.	Mn present. Per cent.	Mn found. Per cent.
0.415	0.423	...	
0.415	0.414	...	
0.415	0.414	1.00	0.990
0.415	0.420	1.00	0.989
0.442	0.440	1.00	0.982
0.442	0.460	1.00	0.980
0.442	0.460	1.00	1.010

LABORATORY OF THE E. AND G. BROOKE IRON CO.,
BIRDSBORO, PA.

THE RAPID DETERMINATION OF CARBON BY COMBUSTION.

BY GEORGE AUCHY.

Received September 5, 1900.

SOME experiences with the dry method of combustion having led the writer to the suspicion that the employment of a rapid rate of gas flow is occasionally attended with loss on account of incomplete oxidation by the copper oxide of the products of ignition and combustion, it was thought that it might be advantageous to use the Shimer apparatus with the modification of having the copper oxide in the crucible instead of in a tube.

In this plan the products of combustion are not forced through the copper oxide by the current of oxygen, but are carried in through the apparatus by the current of oxygen *after* oxidation by the copper oxide has been effected. Therefore, the time of contact with the copper oxide is entirely independent of the rate of gas flow employed, and the carbon compounds will be just as thoroughly oxidized by the copper oxide with a fast as with a slow rate. The carbon dioxide is formed and driven to the top of the layer of copper oxide by the heat of the blast-lamp. Is this period of contact with the copper oxide sufficient for complete oxidation? If so, the rapidity of the passage of oxygen is limited only by the capacity of the potash solution to absorb carbon dioxide rapidly and completely. With solution of 1.400 sp. gr. this capacity is very great.

This plan of having the copper oxide in the crucible had been tried by Dr. Shimer himself who in his original article speaks of

an experiment in which the carbon sponge was covered with asbestos coated with copper oxide. The result, however, was a little low. It seemed to the writer to be worth while to do more experimenting in this direction. A new form of large size crucible was used. The one-half-hour-dried carbon residue and asbestos felt of good thickness, which had previously been transferred (without disturbing its shape) from a Hirsch funnel, smallest size, into a small watch-glass for drying, was transferred to the crucible, *carbon side up*[1]; the wad of asbestos used for cleaning out the funnel was placed to one side; both were pressed down evenly on the bottom by a thick glass rod with a spread-out end; the crucible was filled to nearly the point of reaching the inlet tube of the stopper when in position, with finely ground copper oxide freed completely from carbon, and thoroughly tested in this particular by preliminary blank tests; the copper oxide tube was omitted altogether; the blast-lamp was used for ignition, and purified oxygen (air should also serve) was used at a four- or five-bubble rate, allowing ten minutes for the combustion; the oxygen was used throughout, and the potash bulb was weighed filled with oxygen.[2] The following results were obtained:

No.	Regular combustion, 1-bubble rate. Carbon, per cent.	Shimer modified, 4- to 5-bubble rate. 10-minute combustion. Carbon, per cent.
3886	0.85	0.84
3642	0.96 0.95	0.95 0.96
3906 S	1.16	1.145
3819	1.015	1.00
3921	1.13	1.115
3818	1.11	1.12 1.115
3910	1.46 1.46	1.45

[1] After the last washing of the carbon sponge, some of the copper oxide (3 spoonfuls—smallest size horn spoon) diffused in water was poured on and sucked down.

[2] This was proposed by Dr. Dudley who, however, deprecates the use of this plan in important work. In this the writer must disagree with him. But there is a precaution to be observed in this connection. When the bulbs filled with oxygen stand over night they lose weight, probably because of diffusion between the air on the outside and the oxygen within. We have found this loss to be about 0.0030 gram, but it would doubtless vary somewhat in different cases. A correction for this loss must be applied to the first combustion each morning, or, better, the bulbs should be filled with oxygen before use, whenever they stand for some time between successive combustions.

No.	Regular combustion, 1-bubble rate. Carbon, per cent.	Shimer modified, 4 to 5-bubble rate. 10-minute combustion. Carbon, per cent.
3911	0.79	0.795
3868	1.005 0.995	0.99
3954 L 2	1.12	1.105
3952	0.86	0.85
3979 S	0.925	0.19
1.03 S	1.03	1.034
3995	0.90	0.90
3996	0.925	0.92
3697	1.24	1.235
3697 S	1.245	1.245
3685	0.99	0.98
1.08 Std.	1.08	1.086
3929	0.765	0.76
3982	1.06	1.065 1.07
3989 S	1.04	1.025
3991	1.005	0.99
3988 L 2	1.13	1.14

These results, for practical purposes, are very fair indeed. The results are, on the average, 0.007 per cent. low. The doing away with the copper oxide tube is a gain in simplicity.

It was thought that possibly the copper oxide in the crucible, on account of its finely ground condition, might act as an absorbent for the chlorine and hydrochloric acid of the carbonaceous residue. The 1.03 carbon standard was determined with the glass bead tube (the hydrochloric acid absorbent) omitted, result, 1.03 per cent., indicating that all the hydrochloric acid and chlorine is absorbed by the finely ground copper oxide, and that the glass bead tube may therefore also be dispensed with. It would, however, require a considerable number of tests to prove conclusively that all the hydrochloric acid is retained in the crucible in every case. In the meantime, it is some gratification to know that the copper oxide at least helps to absorb it.

In the original Shimer method, the asbestos is placed in the crucible, carbon side down. It might be thought that in using this modification in order to insure a complete combustion, it would be well to make the asbestos layer as thin as possible.

The writer at first, in filtering, covered the asbestos with a layer of the copper oxide, and at the end of the filtration scraped off the

carbon and copper oxide from the asbestos, and placed these in the crucible directly in the bottom and to one side of the asbestos. But in this plan the volatile portion of the carbonaceous residue seems to be driven off before the copper oxide has become sufficiently heated. Results 0.03 per cent. low were obtained in this way in cases of steel which by the process directed above came either right, or only 0.015 low. A good layer of asbestos seems therefore essential, and the writer also makes it a point not to dry thoroughly previous to combustion, but never longer than one-half hour at 90° C. The copper oxide, is, however, thoroughly dried by a short ignition in a platinum dish or crucible before each combustion.

Besides the results given above, there is other evidence which gives the writer confidence in this process. At these works it is the custom to take two samples from each heat of basic open-hearth steel, determining the carbon (and phosphorus) in each.[1] As these two samples may differ in carbon, a close agreement in the results in any one case, proves nothing, with regard to accuracy of method. But many such agreements—one test regular, the other by the Shimer modified—are entitled to be considered as evidence to the accuracy of the latter process. In cases of disagreement and the Shimer result coming low, the latter for a while were repeated by the regular process, and the results of the above table were for the most part obtained in this way.

This plan has now been abandoned on account of risk of getting into "hard" or "soft" spots twice in succession. We now mix together equal weights of drillings from six different samples (pieces of runner) of a heat, and make one combustion.

It is the writer's custom in his daily work to report carbon results in whole numbers or halves, as the case may be, and this custom has been adhered to in this table.

A very great improvement in connection with the carrying out of carbon determinations, and one which once tried will not be abandoned, is Dr. Sargent's plan of rechlorinating the used double

[1] In cases of a greater variation than 0.06 per cent. a third sample (or fourth, if necessary) is taken. The average is taken, not of all the samples, but only of the two whose results agree within 0.06 per cent. The other, or others, are ignored, experiments having indicated that they are merely "hard spots" or "soft spots" as the case may be. Our experience is in agreement with Wahlberg's that low and medium carbon steels are more apt to vary than high carbon steels, and that phosphorus is more likely to vary than carbon.

chloride solution. There is, however, a source of error connected with its use that deserves to be known.

It would seem that solution of drillings should not be accomplished by allowing to stand at rest over night, except a brisk current of air, or brisk stirring by the machine be first used to drive off free chlorine. A current of air, or brisk stirring, will drive off the chlorine before it has time to do any harm to the separated carbon.

LABORATORY OF HENRY DISSTON AND SONS' STEEL WORKS,
PHILA., PA.

NOTES.

Filtration in Determination of Crude Fiber.—All analysts of food products, or feeding-stuffs, are familiar with the difficulty which is often experienced in filtering off the acid and the alkaline extracts in the determination of crude fiber by the official method of the Association of Official Agricultural Chemists. Hence, I wish to suggest the following modification of the usual procedure, which I have found to give very satisfactory results.

Select a funnel of sufficient size to contain the entire bulk of the mixture to be filtered and fit into its point a small platinum filtering cone. Introduce enough ignited asbestos wool to fill the cone a little more than full. Upon moistening, the asbestos wool softens into a fluffy mass which may be drawn down by suction into a close firm filter. The mass to be filtered is now poured into the funnel with the usual care to avoid disturbing the asbestos layer, and suction applied. The filtrate obtained in this manner has always been found to be free of suspended particles of fiber. Filtration is very rapid except when working with finely ground flour, or spices, which tend to clog the filter and impede the flow of the filtrate. In such cases, place the funnel in an ordinary jacket of boiling water or steam, in order to secure hot filtration, transfer the entire mass to be filtered to the funnel and apply suction as usual. The filtration will then proceed at the proper temperature and without further attention from the operator, thus avoiding the two chief objections to the use of the Gooch filter as recommended by the official method. After filtration and washing are completed, transfer the contents of the funnel to a platinum dish,

rinsing the last particles of fiber from the funnel to the dish by means of a fine jet of distilled water. Evaporate off the water thus used, dry to constant weight, and complete the determination as usual.

I prefer this mode of operation to the use of a paper filter, with correction for loss of weight sustained by the paper in a blank determination, as suggested by Winton,[1] for the reason that in addition to the possibility of obtaining additional fiber from the paper used in the acid filtration, I have found that duplicate determinations of the correction to be applied do not always give concordant results, probably because of variations in the weight or composition of individual filters in any given pack of them. Hence, the correction as obtained from a blank determination may not always be a true one and a corresponding error may be introduced in the final computation.

I have used the method outlined above for several years and upon a great variety of samples, with uniformly satisfactory results. In the cases where filtration is slow it proceeds without attention from the analyst, thus relieving the tediousness of the operation very materially. This method of procedure is especially well adapted to the filtration of the glycerol-sulphuric acid mixture used in the König method for determining crude fiber, since in this case hot filtration is imperative.

R. W. THATCHER.

WASHINGTON AGRICULTURAL COLLEGE AND SCHOOL OF SCIENCE,
PULLMAN, WASH., September 18, 1902.

A Rapid Method for Separating Zinc and the Alkaline Metals from Iron.—The separation mentioned by J. W. Rothe[2] has long been used in the determination of aluminum and nickel and I find that it is equally applicable to the separation of zinc, calcium, magnesium, sodium and potassium from large percentages of iron.

Determination of Zinc.

Having the sample (thoroughly oxidized) in solution in the minimum amount of hydrochloric acid (sp. gr. 1.1), transfer to a separatory funnel, add ether and shake well for about eight

[1] Connecticut Agricultural Experiment Station Report, 1898, p. 189; also Bulletin 65, Bureau of Chemistry, U. S. Department of Agriculture, pp. 58, 154, and 155.

[2] Mittheilungen aus den Königlich. Tech. Versuchs-anstalten zu Berlin," 1892, Part III.

minutes. On standing, the lower solution will contain all of the copper and zinc together with a small amount of ferric chloride. Draw off the lower solution, precipitate the copper with hydrogen sulphide, oxidize with a little bromine and precipitate the small amount of iron. The solution is then ready to determine zinc by any approved method. As many zinc ores contain lead, the effect of sulphuric acid was determined. An excess of 3 cc. had no effect on the separation as long as hydrochloric acid was present. In the presence of lead it is better to separate the lead as lead sulphate before making the ether separation, otherwise lead chloride is liable to clog the cock of the separatory funnel. This single separation is very rapid and more effective than a double basic acetate or triple ammonia separation. The separation of the alkaline metals and aluminum from large amounts of iron, as in the complete analysis of iron ores, is made in the same manner as the above. It has the advantage of rapidity and accuracy, and avoids the excessive amount of salts which are always present when basic acetate or ammonia separations are made. H. C. BABBITT.

NEW BOOKS.

THE MINERAL INDUSTRY: ITS STATISTICS, TECHNOLOGY, AND TRADE IN THE UNITED STATES AND OTHER COUNTRIES TO THE END OF 1901. Founded by the Late RICHARD P. ROTHWELL. Edited by JOSEPH STRUTHERS, PH.D. Vol. 10, xxx + 932 pp. New York and London: The Engineering and Mining Journal (Inc.). 1902. Price, $5.00.

This valuable annual publication has appeared since 1892, and is a treasury of information for those interested in the economic side of chemistry and metallurgy. A somewhat extended account of the contents of the present volume would seem, therefore, to be not out of place here.

The total value of the mineral and metal output for 1901 was $1,372,826,102. Among these products pig iron takes the lead, then follow bituminous and anthracite coal, copper, clay products, gold, iron ore, crude petroleum, stone for building, silver, lead, ferromanganese, cement and natural gas in the order named.

It is stated that there has been a falling off in the production of bauxite, but the total consumption was greater than that of 1900. The Pittsburg Reduction Company is erecting a large plant at

Saline County, Arkansas. A large deposit has been discovered in California.

In the manufacture of aluminum the costs are as follows: Energy, 5 cents; alumina, 6 cents; electrodes, 2 cents; chemicals and stores, 1 cent; labor and superintendence, 3 cents; interest and maintenance, 3 cents; total cost, 20 cents. By the use of the Hall process for refining, the cost of alumina is expected to be 2 cents per pound. This saving, with the consequent reduction in price, is a matter of considerable importance and will enable the metal to be sold at a considerable decrease in price. Two noteworthy changes have been made in the corundum industry during 1901. One, the manufacture of an artificial corundum, and the other the development of corundum deposits in Gallatin County, Montana. Cryolite was imported by the Pennsylvania Salt Manufacturing Co. to the extent of 5,383 tons. The value is stated to be $80.00 per ton. The total production of Greenland cryolite was in 1900, 8,960 metric tons.

The sole producer of aluminum in the United States is the Pittsburg Reduction Company, of Niagara Falls, N. Y., and the production for 1901 was 7,150,000 pounds. The metal has been introduced largely in electrical work in place of copper. New works for the production of this material have been established at Shawinigan Falls in Canada. Experience in the use of aluminum as a conductor has shown that it does not resist exposure as well as copper. The metal is now sold at a price of 33 to 37 cents per pound for 99 per cent. metal.

Of the total 523,000 metric tons of ammonium sulphate produced during 1901, 66,000 tons belong to the United States. This is an increase of over 2,000 tons and is mainly accounted for by the increase in the number of by-product coke ovens now operated.

Three hundred short tons of arsenious oxide were made during 1901 by the Puget Sound Reduction Co., Everett, Washington. This is the only producer in the United States. The product is satisfactory in quality and likely to meet the local western demand. It is possible that the producers may be able to have the tariff changed so as to increase the domestic price for arsenic, in which case it may be possible to carry this product around Cape Horn for the New York market at a profit.

An interesting history of the asphalt industry is given by A. W. Dow.

The production of barytes was 49,070 short tons. The use of this material has increased considerably in the manufacture of barium oxide by the Bradley and Jacobs process at Niagara Falls. This increased amount of barium dioxide is used in the manufacture of hydrogen dioxide, and of lithophone.

During the year, the production of crude carborundum was more than doubled, and the consumption for 1902 shows a large estimated increase. This material is to be of considerable importance in the manufacture of window glass in continuous sheets, by a process now being worked out by parties interested in the glass industry.

The production of Portland cement during 1901 has shown a marvelous increase. Foundations for houses, sidewalks, curbs, cement floors for fire-proof buildings, and the like constitute the source of the largely increasing demand. Over 7,000,000 barrels were made in Pennsylvania and nearly 13,000,000 in the United States.

An interesting account of fire-clays and their manufacture into refractory materials is given by Heinrich Ries. A valuable article on the by-product coke industry is contributed by F. Schniewind, and there is an article on gas producers and gas engines by William Kent.

The Neill process for leaching copper ores does not seem to have passed the experimental stage. The chief difficulty connected with its use seems to lie in the fact that the precious metals are not extracted by sulphurous acid. In other respects the process seems to be quite satisfactory.

There is a valuable article on progress in the electrolytic refining of copper by Titus Ulke, and another on the treatment of slimes from the electrolytic refining of copper by Robert L. Whitehead and a very valuable detailed account of the manufacture of blue vitriol by Ottokar Hofmann. Progress in electro-chemistry and metallurgy is covered in a report by John B. C. Kershaw.

There is a valuable, though rather brief article on commercial hydrofluoric acid by Karl F. Stahl, who has installed at Pittsburg

an admirable plant for the production of this very disagreeable and dangerous chemical.

There is a report on progress in gold milling by R. H. Richards and another on the cyanide process by J. S. C. Wells.

The manufacture of artificial graphite at Niagara Falls has increased enormously, 2,500,000 pounds having been produced in 1901 as against 860,000 pounds in 1900. The production of graphitized electrodes especially has shown a very large increase.

During the last few years there has been a marvelous increase in the production of pig iron and steel in the United States. In 1901 there were 16,000,000 tons of pig produced, and of steel over 13,000,000 tons. Of this, nearly 9,000,000 tons were Bessemer and over 4,000,000 open-hearth. The iron ore production was nearly 29,000,000 tons, to which the Minnesota mines contributed over 11,000,000. This year the production from this source seems likely to be very greatly increased.

An article on modern improvement in the manufacture of pig iron by John Birkinbine gives a clear view of the changes in recent practice.

There are articles on white lead manufacture by Parker C. McIlhiney, and recent improvements in lead smelting by H. O. Hofman.

Manganese ores for the production of ferromanganese are obtained from Colorado, Georgia, Virginia, Belgium, Brazil, Canada, Chili, Colombia, Cuba, France, Germany, Greece, India, Italy, Japan, Java, Russia, Sweden, and Spain. There is an article on the Nicopol manganese district in southern Russia by Frank Drake.

The production of natural gas and its use as a fuel and as a source of power in gas engines receives attention in an article by F. H. Oliphant.

Under cyanides from atmospheric nitrogen, allusion is made to the Bradley-Jacobs patent, which consists in coking barium carbonate and small coal. This porous mixture is next converted in the electric furnace into barium carbide. By passing nitrogen gas over this, cyanide is formed.

Rare elements are treated by Victor Lenher, and under the contact process of sulphuric acid, the article by R. Kneitsch, which recently appeared in the *Berichte,* is fully translated.

It would take up too much space to give anything like a full résumé of the contents of this interesting digest of progress. I must content myself with calling attention further to excellent articles on zinc, pyritic smelting, metallography, mine timbering, alloys as solutions, ore dressing, liquefied carbonic acid gas and magnetic separation. The volume ends with a number of statistical tables. EDWARD HART.

INORGANIC CHEMISTRY, WITH THE ELEMENTS OF PHYSICAL AND THEORETICAL CHEMISTRY. By J. I. D. HINDS, PH.D., Professor of Chemistry in the University of Nashville. New York: John Wiley and Sons. 1902. 8vo. viii + 566 pp. Price, $3.00.

The book, as stated in the preface, is intended to supply a rather complete text-book on inorganic chemistry for colleges and universities, and a handy reference book for all students and teachers of chemistry. Opinions should not differ widely as to how well the author has accomplished either of these objects. As far as the former is concerned, the method adopted is almost entirely that of the most objectionable style of dogmatic instruction: laws, hypotheses, definitions are laid down in axiomatic fashion, with scarcely a hint of the broad experimental basis on which they have actually been developed; structural formulas are used from the very beginning with never a word as to the facts which led to their introduction and use; much effort is expended towards making methods of calculation go by rule rather than by reasoning. The reviewer has looked in vain, repeatedly, for the fundamental laws of definite and multiple proportions (!). A discussion of them is promised on p. 57 but diligent search in all but the later chapters of the descriptive part and in the index failed to lead to their discovery!

In a word, not one particle of the beauty of the inductive method, to which chemistry owes its successful development and all its fascination, is left. The student is asked to accept, to believe; his faith and memory are appealed to and cultivated at the expense of his faculty of reasoning and his power of judging at first hand. It is a source of wonder to the reviewer whether any student's interest in chemistry can survive this method of instruction, and how any inherent power of inductive reasoning from fact to hypothesis and law can escape positive destruction. It is con-

ceivable, however, that the method will, unfortunately, find favor in the eyes of some on account of its positiveness and because it is, perhaps, easier to teach dogmatically than to appeal always to the student's judgment and to be prepared with a rational knowledge of facts and their connection to meet convincingly any keen doubter's questions.

The axiomatic statements are not always correct, as, for instance, when it is said on p. 60 that "the atomic weight of an element may be defined as that quantity which combines with one atom of hydrogen"(!) On p. 5 we have the statement that "in gases the molecules repel one another". On p. 61 we have "it has been found that for most substances that can be volatilized without decomposition the vapor density referred to hydrogen is just half the molecular weight"—it would be interesting to know what the exceptions are. Questionable statements are very numerous.

The second object of the book, *viz.*, to serve as a reference book, seems to the reviewer to be more worthy of success than its first object. The descriptive part is good. It includes quite a large number of historical facts and it gives briefly methods of preparation and manufacture for a large number of compounds. The newest important methods are, however, frequently missing. For instance, the absence of any mention of the electric methods of preparing alkalies, chlorates and hypochlorites and of the contact method of manufacturing sulphuric acid is noted. There is a good index.

CHICAGO, October 20, 1902. JULIUS STIEGLITZ.

ACHT VORTRÄGE ÜBER PHYSIKALISCHE CHEMIE. GEHALTEN AUF EINLADUNG DER UNIVERSITÄT CHICAGO, 20. bis 24. Juni, 1901, von J. H. VAN'T HOFF. BRAUNSCHWEIG: F. Vieweg und Sohn, 1902. 15 × 18 cm. 81 pp. Preis: geheftet Mk. 2.50.

These eight lectures, delivered on the occasion of the decennial celebration of the founding of the University of Chicago, are divided into four groups, each consisting of two successive discourses. The subjects treated are the relation of physical chemistry (1) to chemisty, (2) to the industries, (3) to physiology, and (4) to geology. The author considers that the new developments of physical chemistry rest upon the theory of solutions, being essentially an extension of Avogadro's hypothesis to solutions,

and upon the application of thermodynamics, especially of the Carnot-Clausius principle, to chemical problems. The theory of solutions and the dissociation theory of Arrhenius receive consideration in the first and third groups of the lectures, which give a good brief presentation of the theories and what is claimed for them, without, however, even suggesting that there are now many facts known that do not support these hypotheses. Concrete illustrations are given throughout the entire discourses, which are of the character of general outlines. The brief, concise presentation of the author's splendid researches on natural salt deposits is especially interesting and instructive, particularly so because the work was accomplished without the aid of the theory of solutions and the Arrhenius hypothesis. On the part of those readers who do not have an elementary knowledge of physical chemistry, these lectures will require careful study in order to be fully comprehended.

LOUIS KAHLENBERG.

THE CHEMISTRY OF THE TERPENES. By DR. F. HEUSLER, Privat-docent of Chemistry in the University at Bonn. Authorized translation by DR. FRANCIS J. POND, Assistant Professor in the Pennsylvania State College. One vol., 457 pp. Carefully revised, enlarged, and corrected. Philadelphia: P. Blakiston's Son and Co. 1902. Price, $4.00.

The word terpene seems first to have been used by Kekulé. Such words as terebentene, terebene, terpilene, etc., were coined by French chemists to designate the hydrocarbon now known as pinene and its isomers into which it could be converted, *e. g.*, by heat or acids. Some of these terms acquired a generic as well as a specific meaning. The advantage of a word without a double meaning must have been apparent when Kekulé suggested the word terpene, for it soon came into general use.

However, since Baeyer extended the principles of the Geneva Congress nomenclature to the terminology of the terpenes, the word terpene has also acquired a double meaning. On the one hand it is still used in its larger sense comprising all hydrocarbons $C_{10}H_{16}$; on the other, its use has been specialized, restricting it to those hydrocarbons $C_{10}H_{18}$ which are tetrahydro-derivatives of cymene. It is in the former, broader sense in which the term is used in the book before us.

Although substances containing all the way from one to twenty

and possibly more carbon atoms have been found in volatile oils, it is nevertheless remarkable that a large number of volatile plant substances are characterized by ten carbon atoms or a multiple thereof. Whatever significance may attach to this number, this much is true, that the "terpenes and camphors" have always received a larger share of attention than other volatile plant substances.

The secret of this seems to lie in the fact that the terpenes proper and their derivatives occupy places in that enormous field between the series of hydrocarbons and their derivatives belonging to the formula of saturation C_nH_{2n+2} on the one hand and the formula of saturation C_nH_{2n-6} on the other. The study of the terpenes and their derivatives has done fully as much as any one other subject, if not more, to make this vast *terra incognita* of a few decades ago better known. Incidentally these researches have thrown much new light on phyto-chemistry and the manufacture of volatile oils and of perfumes.

The arrangement of the book is that of the German original. The English edition, however, has been made much more valuable by the incorporation of the vast number of facts published since the appearance of Dr. Heusler's monograph. The number of terpenes described is twenty-two, the number of sesquiterpenes, fourteen.

The number of alcohols, ketones, amino derivatives, etc., has increased proportionately. To the same degree to which Dr. Heusler's monograph was indispensable to the investigator five years ago, to the same extent, and even more so, will Dr. Pond's larger work be indispensable to-day. Moreover, it will prove more satisfactory, for the type is larger, the page is better arranged, the references are more handy, and the book is provided with an index. Thus, while Heusler's work was indispensable to the specialist, the English work will prove useful also as a reference work to the non-specialist. EDWARD KREMERS.

HANDBOOK OF TECHNICAL GAS ANALYSIS. BY CLEMENS WINKLER. Translated from the third greatly enlarged German edition by GEORG LUNGE. London: Gurney and Jackson. 1902. 190 pp.

This book is more than the title indicates as it gives Professor Lunge's description of his own apparatus and in many cases his

experience. It deals very fully and satisfactorily with the subjects of the collection and measurement of gases, the preparation of reagents and arrangement of a laboratory.

Two-thirds of the volume is devoted to the apparatus and methods of analysis, almost every important apparatus and method being clearly and minutely explained together with a critique of the various modifications which have been proposed. In many cases a brief historical notice lends interest to the description.

While the references to German periodicals are very complete, the same cannot be said regarding English or American literature, no mention being made of the work of Clowes, of Phillips, of Campbell and Hart and others.

An admirable feature of the work is the attention given to the applications of the methods: it would have seemed better to have included the method of calculation of the losses in chimney gases —a very important subject—than to have referred the student to other books.

Nearly every process is illustrated by examples from practice but it seems somewhat incongruous in a work on *technical* analysis to report the constituents sought to hundredths of a per cent. as is done in nearly every case. Inasmuch as the readings were taken only to tenths of a per cent. and some of the methods are accurate to only half of one per cent., the hundredths must have been obtained arithmetically.

It is, however, a book which should be in the hands of every one having to deal extensively with the analysis of gases.

A. H. GILL.

METHODS OF GAS ANALYSIS. By DR. WALTHER HEMPEL. Translated from the third German edition and considerably enlarged, by L. M. DENNIS. New York: The Macmillan Co. 1902. xix + 490 pp. Price, $2.25.

This well-known book has been very considerably enlarged and improved by Professor Dennis. Not only has the entire work been thoroughly revised and brought up to date but a number of new forms of apparatus and new methods of analysis have been incorporated. The text has been increased by more than one hundred pages. Some of the new methods are: the separation of argon from the atmosphere, the analysis of acetylene, examination

of gases produced by bacteria, new methods for determining carbon monoxide, determination of the heating power of gases, of sulphur in organic substances, the gas lantern, analysis of the gases evolved in the electrolysis of chlorides and in the manufacture of bleaching-powder.

In its new form this work will undoubtedly come to be regarded as the standard text-book and reference book on gas analysis and will be found indispensable in all chemical laboratories.

EDWARD H. KEISER.

SEWAGE WORKS ANALYSES. BY GILBERT J. FOWLER, M.Sc. (Vict.) F.I.C. Superintendent and Chemist, Manchester Corporation Sewage Works. New York: John Wiley and Sons. London: P. S. King & Son. 1902. Price, $2.00.

With the development of bacterial processes for the treatment of sewage, has arisen the necessity for constant and careful control of the working of the bacterial filters, and this can only be done by chemical analysis of the effluent. In order to keep a sewage plant in good working condition the effluent from each bed must be constantly examined, and the amount of sewage to be applied to the bed determined by the results thus obtained. The methods that are used for this purpose by Mr. Fowler, manager and chemist of the Manchester Sewage Works, and by Mr. Scudder, of the Mersey and Irwell Commission, are now published for the first time, and the book, "Sewage Works Analyses," is an important addition to the literature of the subject. The methods for determining free, albuminoid, and organic ammonia, nitrogen as nitrites and nitrates, solids in suspension and solution, absorbed oxygen, dissolved oxygen, chlorine, iron compounds, acidity and alkalimetry, are so fully and carefully described, that it would be possible for one who has had very little training in chemistry, not only to understand the methods, but to perform successfully the various determinations. It may, however, be well to call to the attention of those not familiar with sewage analysis, that the English method of determining the oxygen consumed, with potassium permanganate and potassium iodide, is not usually used in this country, but in its place, a modification of Kubel's method, heating a known quantity of the sewage for five minutes with a solution of potassium permanganate, and determining the amount of potassium permanganate used by titrating with oxalic acid;

that of the three methods given for the determination of dissolved oxygen, the indigo method, in the opinion of the writer, though more complicated, gives the best results, and that the colorimetric methods for the determination of ferrous and ferric salts, can only be considered as approximate methods.

Beside the various determinations that have been mentioned the author devotes a chapter of the book to the subject of Chemical Control of Sewage Purification Works, in which he also describes methods for gauging sewage flow, methods of sampling sewage, measuring of sewage sludge, and of determining the degree of purity necessary in an effluent, and in this connection it is to be said that the incubator test, devised by Mr. Scudder and given in detail by Mr. Fowler, is one upon which great importance is now laid, in determining whether or not a sufficient purification of the sewage has been accomplished. The concluding chapter of the book is devoted to the collection and analysis of the gases given off from septic tanks and contact beds, and it is to be regretted that no mention is made of Hempel's methods of gas analysis, which are now so commonly used. Taking the book as a whole, very much can be said in its favor and very little in the way of criticism. LEONARD P. KINNICUTT.

CONGRÈS INTERNATIONAL D'ÉLECTRICITÉ, PARIS, 1900; par M. E. HOSPITALIER. Paris: Gauthier-Villars. 1901.

This large 8mo. of nearly 500 pages contains the reports and proceedings of the congress. The third section of the congress was devoted to electrochemistry, but the communications on this subject occupy but 22 pages. They include a discussion of the electrochemical nomenclature proposed by Dr. Le Blanc, in which the proposition was generally rejected; a notice of papers by Hollard on the principles of electrolytic analysis and analysis of commercial copper; a short communication of Zenger on the use of sea-salt mother-liquor in a battery cell; a very fragmentary paper by Bouillet on electrochemical deposits; and a paper of 15 pages by Keller on electric furnaces. The above comprises all in the book which touches chemistry, excepting possibly a careful report by G. Claude (23 pp.) on the mechanism of electrolysis by street-railway return-currents. The volume would be out of place in a chemical library, but contains matter of value to the professional electrician. J. W. RICHARDS.

Issued with July Number, 1902.

Proceedings.

BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the Chemists' Club, 108 W. 55th St., New York City, Friday, May 23, 1902. The directors present were Messrs. Chandler, Doremus, Hale, Hallock, and Smith. Messrs. Remsen and Dudley sent regrets for unavoidable absence.

In the absence of President Remsen, Secretary Hale called the meeting to order at 8.45 P.M., and Dr. C. F. Chandler was chosen chairman *pro tem.*

Mr. Wm. H. Nichols was present and proposed to transfer to the American Chemical Society in trust for the New York Section ten shares of the preferred stock of the General Chemical Company to constitute the endowment fund for medals which he had offered to the New York Section at its last meeting, and which had been accepted by said section. In response to this proposal of Mr. Nichols, the following resolutions were adopted unanimously:

Resolved, "That the Board of Directors of the American Chemical Society, acting for and in behalf of said Society, hereby accepts the liberal gift of Mr. Wm. H. Nichols of an endowment fund for medals to be awarded by the New York Section, under the terms designated in the deed of transfer to the American Chemical Society executed by the said Wm. H. Nichols.

Resolved, "That the president and the secretary of the American Chemical Society be, and they are hereby, authorized and directed to sign the said deed of transfer for and in behalf of the Society as evidence of the acceptance by the Society of the said endowment fund under the terms stated in said deed of transfer.

Resolved, "That the Board of Directors in behalf of the American Chemical Society hereby expresses its cordial thanks to Mr. Nichols for his generous gift and its high appreciation of the spirit which prompted it."

Mr. Nichols wished it expressly understood that he would personally defray all costs of die and other incidental expenses connected with the manufacture of the medal.

The secretary was instructed by the Board of Directors to have its action in regard to the fund printed in the Journal of the Society and sent to the members of the Council.

Professor C. F. Chandler and Professor M. T. Bogert were appointed a committee to confer with Mr. Nichols and arrange all details with reference to the deed of transfer.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Branegan, James A., 981 Bedford Ave., Brooklyn, N. Y.
Collins, Robert H., Alameda Sugar Co., Alvarado, Cal.
Covell, Chas. A., M.D., Syracuse, N. Y.
Emmons, Frank W., Care Washburn Crosby Co., Minneapolis, Minn.
Fisher, Fred., Newaygo, Mich.
Geer, William C., 122 Hazen St., Ithaca, N. Y.
Hill, Lucian A., Durham, N. H.
Jennings, Fred H., Orchard Place, Ithaca, N. Y.
Lemly, Frederick H., Bio-chemical Lab., Dept. of Agr., Washington, D. C.
Mende, Alex. P., 125 E. 62nd St., N. Y. City.
Miyake, Hanzaburo, 121 Haight St., San Francisco, Cal.
Moss, Eugene G., Tenn. C. I. & R. Co., Bessemer, Ala.
O'Neill, Jas. G., Box 771, Geneva, N. Y.
Porter, Fred B., 4645 Evans Ave., Chicago, Ill.
Read, Thomas T., Univ. of Wyoming, Laramie, Wyo.
Smith, Arthur G., care of Dickman, Mackenzie, and Potter, "The Rookery," Chicago, Ill.
Stearns, Edgar F., 711 Nostrand Ave., Brooklyn, N. Y.
Turrentine, John W., Burlington, N. C.
Weller, Hubert R., Weldon, N. C.
Wheeler, Frank G., New York Mills, Oneida Co., N. Y.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Batchelor, Harry D., West Upton, Mass.
Burck, Christian A., Monroe, Mich.
Snelling, Walter O., 1212 L St., N. W., Washington, D. C.
Stewart, Morris A., 121 Belknap St., Dover, N. H.

NEW MEMBERS ELECTED MAY 22, 1902.

Evanson, A. A., Aetna, Ind.
Gibson, Charles B., Room 39, 81 S. Clark St., Chicago, Ill.
Goslau, Justus E. W., 177 Broad St., Newark, N. J.
Ingham, Leslie H., Kenyon Coll., Gambier, O.
Kalbfleisch, Franklin H., 31 Burling Slip, N. Y. City.
Knight, Ora W., 84 Forest Ave., Bangor, Me.
Langley, Clifford, 64 Irving Pl., N. Y. City.
Lomax, Clarence S., New England Gas and Coke Co., Everett, Mass.
McClure, Clyde H., 724 Forest Ave., Oak Park, Ill.
Moorhouse, Wm. R., Lowell Textile School, Lowell, Mass.
Queneau, Augustin L. J., 439 Manhattan Ave., N. Y. City.
Reed, Charles J., 3313 N. 16th St., Philadelphia.
Richmond, Francis A., Elmira College, Elmira, N. Y.
Starke, Eric A., Pacific Coast Oil Co., Alameda, Cal.
Simonds, Ernest H., 417 Montgomery St., San Francisco, Cal.
Stofer, Richard C., 28 Hayes St., Norwich, N. Y.
Walters, Harry E., 4 Shetland Ave., East Liberty, Pittsburg, Pa.
Williams, Stanley M., 269 Springdale Ave., E. Orange, N. J.

NEW MEMBERS ELECTED JUNE 23, 1902.

Aydelott, Charles G. B., Maple and Ridgewood Aves., Norwood, O.
Brady, Wm., 7642 Marquette Ave., Chicago, Ill.
Burr, H. M., 165 Prospect Park West, Brooklyn, N. Y.
Campbell, A. H., 813 20th St., Oakland, Cal.
Clay, G. Harry, Winton Place, O.
Devlin, John A., Newton, Kans.
Doveton, Godfrey D., Cyanide Works, Camp Bird Mills, Ouray, Col.
Dunham, Andrew A., 74 John St., N. Y. City.
Haas, Herbert, Torreen, Coahuila, Mexico.
Hermes, Edward, 979 Parsons Ave., Columbus, O.
Hewett, Foster, 66 Church St., Bethlehem, Pa.
Kawin, C. C., 1424 Fulton St., Chicago, Ill.
Lindauer, Arthur M., 3312 Calumet Ave., Chicago, Ill.
Lippincott, Jesse T., 261 E. Auburn Ave., Cincinnati, O.
Ludlow, S. H., Cement City, Mich.
Meyer, August R., 404 New England Building, Kansas City, Mo.
Miller, Robert N., Male High School, Louisville, Ky.
Mott, Wm. A., Mayfield, Ky.

Neal, A. Frank, care of Acme White Lead and Color Works, Detroit, Mich.
Petsche, B. W., 25 Fairview St., Yonkers, N. Y.
Putnam, Wm. P., care of American Radiator Co., Chicago, Ill.
Randall, Charles W., 228 Genesee St., Lockport, N. Y.
Rich, Charles H., Duquesne, Pa.
Richardson, Leon B., Hanover, N. H.
Roe, J. Newton, Valparaiso, Ind.
Rogers, Roy R., 2528 Union St., San Francisco, Cal.
Rounds, M. B. C., Aurora, Ill.
Schwarz, H. P., Western Sugar Ref. Co., Potrero, San Francisco, Cal.
Smith, Robert C., 425 Home Ave., Oak Park, Ill.
Stoddard, Jesse D., care of Operating Board, American Radiator Co., Chicago, Ill.
Vannier, Charles H., 1623 Fulton St., Chicago, Ill.
Waldenberger, Charles A., 155 E. 37th St., N. Y. City.
Wilson, R. N., Guilford College, N. C.
Witherell, Frederick W., care of Newcastle Water Co., Newcastle, Pa.

ASSOCIATES ELECTED JUNE 23, 1902.

Haines, J. Hilyard, 2130 S. 15th St., Philadelphia, Pa.
Thomas, Elmer L., 31 Nassau St., N. Y. City.

CHANGES OF ADDRESS.

Aldridge, Earl V., 413 Church St., Flint, Mich.
Allen, Lucius E., Crescent Portland Cement Co., Wampum, Pa.
Alway, F. J., Waterford, Ontario, Can.
Baxter, G. P., 27 Warren Ave., Somerville, Mass.
Beck, Herbert H., F. and M. College, Lancaster, Pa.
Betts, Anson G., Troy, N. Y.
Bird, Maurice, Denver, Colo.
Bixby, Geo. L., The Willard Storage Battery Co., 49 Wood St., Cleveland, O.
Blair, Frank W., "The Alexandra," Schenectady, N. Y.
Brown, C. Arthur, 218 Washington St., Lorain, O.
Brush, Chas. F., "The Arcade," Cleveland, O.
Burleigh, Wm. F., 5 Monmouth Pl., Newark, N. J.
Button, O., 522 Trumbull Ave., Bay City, Mich.
Corse, W. M., 25 Hendrie Ave., Detroit, Mich.
Craig, A. G., 377 W. 125th St., N. Y. City.
Doan, (Miss) Martha, Vassar College, Poughkeepsie, N. Y.
Dunlap, F. L., 717 Arbor St., Ann Arbor, Mich.

Eccles, David C., 191 Dean St., Brooklyn, N. Y.
Edgar, C. G., 72 Jefferson Ave., Detroit, Mich.
Ellis, Carleton, Room 37, 235 Washington St., Boston, Mass.
Ely, Chas. R., Frederick, Md.
Escher, Paul, 1332 South Ave., Niagara Falls, N. Y.
Felt, W. W., 6312 Parnell Ave., Chicago, Ill.
Fernberger, H. M., 1939 N. 12th St., Philadelphia, Pa.
Fosdick, E. H., 828 E. 3rd St., Los Angeles, Cal.
Fritchle, O. P., 1618 Pennsylvania Ave., Denver, Colo.
Gass, James K., 413 Vanhook St., Camden, N. J.
Getz, Wm. H., 5433 Vernon Ave., St. Louis, Mo.
Godley, Geo. McM., N. J. Zinc Co. (of Pa.), Palmerton, Pa.
Goessmann, C. I., 721 Pleasant St., Worcester, Mass.
Graham, J. Howard, 1309 Erie Ave., Philadelphia, Pa.
Hall, Roy D., Burnett Junction, Wis.
Hamilton, L. P., Dunbar, Pa.
Harding, E. P., 1316 7th St., S. E., Minneapolis, Minn.
Hartzell, L. J., Box 6, Philipsburg, Mont.
Hazard, F. R., Box 2, Syracuse, N. Y.
Hershey, Elam, Care Northern Iron Co., Port Henry, N. Y.
Hicks, Edwin F., 361 W. 27th St., N. Y. City.
Hovey, Will C., 143 and 145 Lake St., Chicago, Ill.
Howard, A. P., 77 Broad St., Boston, Mass.
Humphrey, Richard L., Harrison Bldg., Philadelphia, Pa.
Jessurun, David, Wallesburg Sugar Co., Wallesburg, Ontario, Canada.
Jones, L. J. W., 813 Worthington Place, Omaha, Nebr.
Keller, Charles, 117 Biddle Ave., Sta. D., Pittsburg, Pa.
Keller, Cornelius, care of Geo. B. Wardman, Aguascalientes, Mexico.
Kendall, Arthur I., 338 Broadway, Somerville, Mass.
Kendall, E. Dwight, 395 Ocean Ave., Brooklyn, N. Y.
Knorr, Aug. E., Baltimore Copper Smelting and Rolling Co., Canton, Baltimore, Md.
Krayer, Stephen S., Herf & Frerichs Chem. Wks., St. Louis, Mo.
Lachman, Arthur, 1732 Pacific Ave., San Francisco, Cal.
Langley, Clifford, 229 Blatchley Ave., New Haven, Conn.
Lichtenstein, A. F., Box 350, North Adams, Mass.
Mabery, C. F., North Gorham, Me.
Mains, E. E., 582 18th St., Detroit, Mich.
Mason, Francis P., Pittsburgh Plate Glass Co., Frick Bldg., Pittsburg, Pa.
Mathewson, E. P., Anaconda, Mont.
Miller, Armand R., Man. Tr. High School, Kansas City, Mo.
Myers, Ralph E., Chem. Lab., Lake Superior Power Co., Sault Ste. Marie, Ontario.

Osborne, Thos. B., Box 164, New Haven, Conn.
Page, Robt. W., Box 79, Litchfield, Conn.
Pegg, E. F., 100 W. Clinton St., Cleveland, Ohio.
Pemberton, H., Jr., Cape May, N. J.
Perry, Joseph H., 276 Highland St., Worcester, Mass.
Plank, W. F., Box 63, Morgantown, Pa.
Rand, Chas. L., 929 Lafayette Ave., Brooklyn, N. Y.
Reese, Herbert J., Livingston, Mont.
Ritchey, J. C., The Salem Iron Co., Leetonia, O.
Rogers, Allen, Hampden Corner, Maine.
Root, William W., 410 Marshfield Ave., Chicago, Ill.
Seidensticker, L. J., care of Mr. F. J. Seidensticker, 6 Hurlburt St., Cambridge, Mass.
Silverman, Alexander, 803 S. Negley Ave., Pittsburg, Pa.
Simonson, W., 126 W. 9th St., Cincinnati, O.
Skinner, Hervey J., care of Little & Walker, 7 Exchange Place, Boston, Mass.
Smith, Francis P., care of Percy Tarbutt, Esq., 23 St. Swithin's Lane, London, E. C., England.
Smith, Frederic J., 46 Reid St., Elizabeth, N. J.
Stern, David, 108 Garfield Pl., Cincinnati, O.
Titus, (Miss) Winifred, 425 Park St., Madison, Wis.
Trowbridge, P. F., Croswell, Mich.
Tuckerman, Alfred, 1123 Broadway, N. Y. City.
Turner, B. B., Care Mr. E. S. Hall, 127 Forest Ave., Jamestown, N. Y.
Vinson, A. E., 31 Walnut St., Dayton, O.
Warren, Robert C., Armour Packing Co., Armour Station, Kansas City, Kans.
Whitaker, M. C., care of Welsbach Light Co., Gloucester City, N. J.
Wigfall, E. Newton, Lansdowne, Pa.
Wilkins, Albert D., Box 324, Vandergrift, Pa.
Wood, E. F., P. O. Box 1325, 74 Broadway, N. Y. City.
Youtz, L. A., Lawrence Univ., Appleton, Wis.
Zoul, Charles V., 1646 Broadway, Cleveland, O.

ADDRESS WANTED.

Campbell, George F., formerly of Peoria, Ill.

MEETINGS OF THE SECTIONS.

NORTH CAROLINA SECTION.

The sixth annual meeting of the North Carolina Section was

held on Saturday, May 17th, in the office of the State Chemist, Agricultural Building, Raleigh.

The officers elected for the ensuing year were: *President*, Chas. E. Brewer; *Vice-President*, G. S. Fraps; *Secretary-Treasurer*, C. B. Williams; *Councilor*, B. W. Kilgore, and *Executive Committee*, Chas. E. Brewer, G. S. Fraps, and C. B. Williams.

Resolutions were passed in remembrance of Hugh Lee Miller, who died on February 5th.

The program was as follows: "Molecular Attraction," by J. E. Mills; "Bromination of Heptane under Pressure," by A. S. Wheeler; "Notes on the Occurrence of Cobalt in Wake County, North Carolina," by S. E. Asbury; "Action of Chloral upon the Nitranilines," by A. S. Wheeler and H. R. Weller; "The Determination of Starch in Baking-Powders," by W. M. Allen; "Arsenic Pentachloride," by Chas. Baskerville and H. H. Bennett; Separation of Pure Praeseodymium Compounds," by Chas. Baskerville and J. W. Turrentine; "The Sulphur Content of Some Plants," by W. A. Withers and G. S. Fraps; "Determination of Sulphur in Plants," by G. S. Fraps; "Determination of Sulphuric Acid in Soils," by C. B. Williams; "Some New Reactions of Thorium and Allied Elements with Organic Bases," by Chas. Baskerville and F. H. Lemly; "Rediscovery of a Process for Renderi Phosphoric Acid Available," by Chas. Baskerville; "A Bath for Hot Precipitations," by Chas. Baskerville; "A Platinum Air-Bath," by Chas. Baskerville; "Black Rain in North Carolina," by Chas. Baskerville and H. R. Weller.

C. B. WILLIAMS, *Secretary.*

MICHIGAN SECTION.

The Michigan Section met in the convention hall of the Russell House, Detroit, on Friday evening, April 26th, at eight o'clock. About sixty members and visitors were in attendance.

The following papers were presented: "Chemical Architecture," by Dr. J. M. Francis; "Comparison of Methods for Direct Analysis of Beets," by Mr. David L. Davoll, Jr.; "Trivalent Carbon," by Dr. M. Gomberg.

Previous to the meeting there was an informal dinner at the Russell House, with twenty-six present. A communication from

the Michigan Academy of Science was read, proposing an affiliation of all the scientific organizations of the state. The president of the section, Professor Freer, was appointed to represent the section at a conference of societies interested.

ALFRED H. WHITE, *Secretary.*

Issued with August Number, 1902

Proceedings.

TWENTY-SIXTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The twenty-sixth general meeting of the American Chemical Society was called to order by President Remsen, in the chapel of the Bellefield Presbyterian Church, Pittsburg, Pa., at 11.20 A.M., Monday, June 30, 1902.

The minutes of the twenty-fifth general meeting were approved as recorded in the secretary's book.

Reading and discussion of papers was then taken up in the following order:

"Bessemer and Open-hearth Steel Practice," by Edward H. Martin and William Bostwick. Read by Mr. Martin.

"Manufacture of Optical Glass," by George A. Macbeth.

"The Ozone from Potassium Chlorate," by Edward Hart. Read by title.

"Electric Combustion," by Edward Hart.

"Arsenic Pentachloride," by Charles Baskerville and H. H. Bennett.

"A New Method for the Preparation of Pure Praseodymium Compounds," by Charles Baskerville and J. W. Turrentine.

"Deportment of Pure Thorium and Allied Elements with Organic Bases," by Charles Baskerville and F. H. Lemly.

"The Chlorides of Ruthenium," by Jas. Lewis Howe.

After some announcements by the secretary, the session was adjourned.

TUESDAY, JULY 1ST.

The Society was called to order by the president at 9.10 A.M. A few membership statistics were presented by the secretary, after which papers were read and discussed as follows:

"Malleable Iron," by H. E. Diller.

"The Electrical Conductivity and Freezing-Points of Aqueous Solutions of Certain Metallic Salts of Tartaric, Malic, and Succinic Acids," by O. F. Tower.

"The Old and the New in Steel Manufacture," by William Metcalf.

"An Explanation of Quantivalence and of Stereochemistry," by T. W. Richards.

"The Exactness of Faraday's Law," by T. W. Richards.

"Ionic Velocities in Liquid Ammonia Solutions," by E. C. Franklin and H. P. Cady. Read by Mr. Cady.

"A Thermochemical Constant," by F. W. Clarke. Discussed by Messrs. W. A. Noyes, Clarke, and Bancroft.

"Solubility, Electrolytic, and Chemical Action in Liquid Hydrocyanic Acid," by Louis Kahlenberg and Herman Schlundt. Read by title.

"Molecular Attraction," by J. E. Mills. Read by title.

"On Conductivity," by George A. Hulett.

"Relation between Negative Pressure and Osmotic Pressure," by George A. Hulett. Read by title.

"A New Apparatus for Measuring the Coefficient of Expansion of Gases," by T. W. Richards and K. L. Mark. Read by title.

"The Expansion of a Gas into a Vacuum and the Kinetic Theory of Gases," by Peter Fireman. Read by title.

"Electrolytic Deoxidation of Potassium Chlorate," by Wilder D. Bancroft. Read by title.

"The Solid Phases in Certain Alloys," by Wilder D. Bancroft. Read by title.

Upon motion of the secretary, votes of thanks were given unanimously as follows: To the Local Committee of Arrangements, George A. Wardlaw, secretary; Engineering Society of Western Pennsylvania and its committee appointed for entertaining the chemists; managers of the various works and institutions that have been open to the visit and inspection of the chemists; pastor and trustees of the Bellefield Presbyterian Church; Professor Francis C. Phillips; also to the following named gentlemen who presented papers and addresses upon the various manufacturing interests of Pittsburg and vicinity: Edward H. Martin and William Bostwick; George A. Macbeth, H. E. Diller, and William Metcalf.

After a few announcements, the twenty-sixth general meeting of the Society was adjourned.

ALBERT C. HALE, *Secretary.*

COUNCIL.

A meeting of the Council of the American Chemical Society was held in the parlor of Hotel Schenley, Monday, June 30, 1902. The meeting was called to order by President Remsen at 9.40 P.M.

The following named councilors were present: Messrs. Remsen, E. F. Smith, C. B. Dudley, Clarke, Marshall, T. W. Richards, McMurtrie, Parker, Hillebrand, Hale, Morley, Long, Venable, W. A. Noyes, Baskerville, and Talbot.

The minutes of the twenty-fifth general meeting, as recorded in the secretary's book, were approved.

The Council voted that the names of all candidates for membership presented up to the close of the twenty-sixth general meeting, are herewith passed upon favorably by the Council, and the candidates shall be notified by the secretary of their election to membership, whenever all other requirements in their case shall be fulfilled.

It was voted that the next general meeting of the Society shall be held in Washington, D.C., during "Convocation Week" (the week in which the first day of January occurs), upon such days as the president and secretary may determine.

The secretary then presented to the Council the following communication:

"*To the Council of the American Chemical Society:*

"GENTLEMEN.—The American Chemical Society has honored me with the office of secretary continuously since the year 1889. For a few years my position was that of corresponding secretary, but soon the duties of both corresponding and recording secretary were united in the same person and have so continued until the present time.

"These have been years of arduous service, and also years in which much gratification has come to us all.

"In 1889 there were only 204 persons enrolled as members of the Society, the smallest number in its whole history. Since that year the roll of membership has steadily increased, while previous to that date there was a gradual decline for several years. To-day there are 2,020 members in full standing, 50 other persons just notified of their election as members, and there are 26 nominations to membership pending, making a grand total, when all shall have qualified, of 2,096.

"It is not for me to say to what extent the humble efforts of the secretary and his devotion to the welfare of the Society may

have contributed to the sudden and permanent change in its fortunes which is represented by these variations in its membership roll. The repeated endorsement of the record of the secretary by his reelection to the same office year after year, reveals the confidence and support that have been given him, and constitutes a testimonial which he has highly appreciated, and for which he desires to express his heartfelt thanks.

"The time has come now when I must decline a reelection to the office of secretary which I have occupied so many years. The increasing demands of the position require more of time and energy than I can afford to withdraw from other duties both official and personal. I take the opportunity of notifying you at this time of my decision in order that you may be able to mature plans for the successful administration of the office of secretary after the close of this calendar year when the period for which I was last elected shall expire.

"With most cordial and grateful thanks for your confidence and support in the past and assuring the Society, through you, that my interest in its welfare will be deep and abiding, I remain,

"Yours respectfully,

"ALBERT C. HALE.

"*Pittsburg, June 30, 1902.*"

Upon motion of Dr. Edgar F. Smith, it was voted "that a committee of three be appointed by the chair to prepare resolutions appreciative of the long and faithful services of the secretary, who declines to accept reelection at the expiration of the calendar year." The chair appointed as such committee Drs. Smith, Dudley, and McMurtrie.

The secretary called attention to a communication which he had received regarding the compilation of a technolexicon in German, French, and English, and he was authorized to have a notice of the proposed work printed in the Journal and to receive and forward to those having it in charge the names of such persons as shall notify him of their willingness to become colaborers in such work.

Dr. H. P. Talbot presented the following report, which was accepted, and its recommendations adopted:

"The committee appointed to consider the desirability of changes in the system of administration of the Society and in the membership of the Council of the Society, begs to report as follows:

"First. That the committee considers it inexpedient at this

time to recommend any change in the constitution of the Society with reference to the membership of the Council.

"Second. That the committee recommends that the duties of the offices of secretary and editor of the Society be combined, and that the same person be elected to serve in the two offices after the close of the present calendar year.

"H. P. TALBOT,
"*Secretary of the Committee.*"

Upon motion of Dr. McMurtrie it was voted "that the president and treasurer be authorized, in their discretion, to negotiate a loan to meet the necessities of the present year, and to use for collateral, in such case, any securities belonging to the Society other than those covering the life-membership funds."

The editor requested an additional allowance to be inserted in budget of expenses for the current year, as follows: For printing, $1,400; for abstractors, $300. Total, $1,700.

This request was granted, and the Council was then adjourned.

ALBERT C. HALE, *Secretary.*

NAMES PROPOSED FOR MEMBERSHIP.

Breed, (Miss) Mary B., Indiana Univ., Bloomington, Ind.

Carter, William H., Water Bureau, Dept. of Public Works, Pittsburg, Pa.

Gray, G. W., Whiting, Ind.

Hall, Elmon Lawrence, 1613 Gough St., San Francisco, Cal.

Hawk, W. B. N., Elyria, O.

Mallinckrodt, Edward, Jr., 26 Vandeventer Pl., St. Louis, Mo.

Mueller, Edward, Roanoke, Va.

Randel, Frank L., 242 Rutledge St., Brooklyn, N. Y.

Taylor, Edward R., Penn Yan, N. Y.

Watkins, Edwin D., Lafayette College, Easton, Pa.

Wheeler, C. Gilbert, 14 State St., Chicago, Ill.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Outwater, Raymond, 1312 B St., S. W., Washington, D. C.

NEW MEMBERS ELECTED JULY 14, 1902.

Branegan, James A., 981 Bedford Ave., Brooklyn, N. Y.

Collins, Robert H., Alameda Sugar Co., Alvarado, Cal.

Covell, Charles A., Syracuse, N. Y.

Emmons, Frank W., care of Washburn-Crosby Co., Minneapolis, Minn.
Fisher, Fred., Newaygo, Mich.
Geer, William C., 122 Hazen St., Ithaca, N. Y.
Hill, Lucian A., Durham, N. H.
Jennings, Fred. H., Orchard Place, Ithaca, N. Y.
Lemley, Frederick H., Bio-chemical Laboratory, Dept. of Agr., Washington, D. C.
Mende, Alex. P., 125 E. 62d St., N. Y. City.
Miyake, Hanzaburo, 121 Haight St., San Francisco, Cal.
Moss, Eugene G., Tenn. C. I. and R. Co., Bessemer, Ala.
O'Neill, James G., Box 771, Geneva, N. Y.
Porter, Fred. B., 4645 Evans Ave., Chicago, Ill.
Read, Thomas T., Univ. of Wyoming, Laramie, Wyoming.
Smith, Arthur G., care of Dickman, Mackenzie & Potter, "The Rookery," Chicago, Ill.
Stearns, Edgar F., 711 Nostraud Avenue, Brooklyn, N. Y.
Turrentine, John W., Burlington, N. C.
Weller, Hubert R., Weldon, N. C.
Wheeler, Frank G., New York Mills, Oneida, Co., N. Y.

ASSOCIATES ELECTED JULY 14, 1902.

Batchelor, Harry D., West Upton, Mass.
Burck, Christian A., Monroe, Mich.
Snelling, Walter O., 1212 L St., N. W., Washington, D. C.
Stewart, Morris A., 121 Belknap St., Dover, N. H.

CHANGES OF ADDRESS.

Beans, H. T., 2406 N. 21st St., Omaha, Nebr.
Bird, R. M., Univ. of Missouri, Columbia, Mo.
Cady, W. B., Bay City, Mich.
Collins, Ward O., 1322 Hinman Ave., Evanston, Ill.
Eberman, W. S., Sumpter, Oregon.
Ely, Chas. R., Gallaudet College, Washington, D. C.
Escher, Paul, The Provident Chemical Works, St. Louis, Mo.
Evans, Wm. L., 1168 Fair Ave., Columbus, Ohio.
Felt, W. W., 6912 Parnell Ave., Chicago, Ill.
Goodmar, Julian H., care of Joseph Ullmann, 19 Ritter Str., Leipsic, Germany.

Gore, Herbert C., Kent Chem. Lab., Univ. of Chicago, Chicago, Ill.
Gross, John, Box 107, Elyria, Colo.
Haslwanter, Charles, 908 Willoughby Ave., Brooklyn, N. Y.
Haynes, Herman W., East Pepperell, Mass.
Hermes, Edward, Portsmouth, Ohio.
Herty, Charles H., U. S. Bureau of Forestry, Ocilla, Ga.
Hill, Arthur E., Freiburg in Breisgau, Germany.
Kenrick, E. B., 282 Assiniboine Ave., Winnipeg, Canada.
Landon, W. B., Meadville, Pa.
Leach. (Miss) M. F., 802 Oakland Ave., Ann Arbor, Mich.
Mack, J. Lathrop, Craigsville, Augusta Co., Va.
Mersereau, Gail, 130 E. 36th St., N. Y. City.
Miller, Howard E., 134 W. 4th St., Portsmouth, O.
Moore, C. J., Flint Hill, Va.
Mowry, Jesse B., Chepachet, R. I.
Naglevoort, J. B., 702 Champlain St., Detroit, Mich.
Page, Robert W., 527 Third St., Brooklyn, N. Y.
Passolt, H. A., 506 S. Oakley Ave., Chicago, Ill.
Patterson, Austin M., Xenia, O.
Phalen, W. C., National Museum, Washington, D. C.
Reese, Chas. L., care of Repauno Chemical Co., Chester, Pa.
Siedler, George J., 253 Broadway, N. Y. City.
Sloane, T. O'Conor, 35 Broadway, N. Y. City.
Stoddart, Charles W., 1068 York St., Denver, Colo.
Topping, Alanson N., 921 Minn Ave., Kansas City, Kans.
Underwood, Geo. R., 4 Emerson St., Peabody, Mass.
Walker, Percy H., 416 McCluny St., Huntsville, Ala.
Willard, H. H., Union City, Mich.
Wingate, Hamilton, "Glenthorpe," Cotham Grove, Bristol, England.

The Society of German Engineers has undertaken the publication of a Trilingual Technical Dictionary in German, English, and French, to be called the "Technolexicon," and is asking for co-laborers in the various technical branches. A note-book will be sent to each person who indicates his willingness to act as a co-laborer, and he is asked to write down all his contributions and notes in such note-book. The note-book consists of three sections, one for each language, each with an alphabetical index.

On the inside of the cover instructions are given as to using the note-book and thus contributing to the success of the undertaking.

If any members of the American Chemical Society or others, are willing to serve as co-laborers and will signify this, sending at the same time their names and addresses to the Secretary of the American Chemical Society, he will undertake to forward this information to the Society of German Engineers, and the German Society will thereupon send one copy of the note-book to each person who thus expresses his willingness to aid in the undertaking. Address, without delay,

ALBERT C. HALE,
Secretary of the American Chemical Society,
352 A Hancock St.,
Brooklyn, N. Y.

Issued with September Number, 1902.

Proceedings.

COUNCIL.

The Council has approved the following motion offered by Dr. Wiley:

"That the President of the American Chemical Society be authorized to appoint a committee of organization to enlist the collaboration of American chemists in the Fifth International Congress of Applied Chemistry, to be held in Berlin, May 31 to June 7, 1903: that the committee consist of at least ten members representing the ten sections into which the congress has been divided, *viz.*,

1. Analytical chemistry, apparatus and instruments.
2. Chemical industries of inorganic products.
3. Metallurgy and explosives.
4. Chemical industries of organic products.
5. Chemical sugar industry.
6. Fermentation industries.
7. Agricultural chemistry.
8. Hygiene, medicine, pharmaceutical chemistry and food products.
9. Photo-chemistry.
10. Electrochemistry."

NAMES PROPOSED FOR MEMBERSHIP.

Allen, Wm. P., N. J. Agr. Exp. Sta., New Brunswick, N. J.

Fairlie, Andrew M., Detroit Copper and Brass Rolling Mills, Detroit, Mich.

Gray, John H., Jr., 1523 Pt. Lobos Ave., San Francisco, Cal.

Haehnlen, J. L., Otto, Allegheny Co., Pa.

Parrett, Ben C., Lake Superior Power Co., Sault Ste. Marie, Ontario.

Teeple, John E., Cornell Univ., Ithaca, N. Y.

Wheeler, (Miss) May, 802 Oakland Ave., Ann Arbor, Mich.

Woods, Fred. L., 418 South St., Iola, Kans.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Welch, Charles C., Jr., 1450 Washington Ave., Denver, Colo.

NEW MEMBERS ELECTED AUGUST 7, 1902.

Breed, (Miss) Mary B., Indiana Univ., Bloomington, Ind.
Gray, G. W., Whiting, Ind.
Hall, Elmon L., 1613 Gough St., San Francisco, Cal.
Hawk, W. B. N., Elyria, O.
Mallinckrodt, Edward, Jr., 26 Vandeventer Pl., St. Louis, Mo.
Randel, Frank L., 242 Rutledge St., Brooklyn, N. Y.
Taylor, Edward R., Penn Yan, N. Y.
Wheeler, C. Gilbert, 14 State St., Chicago, Ill.

NEW MEMBERS ELECTED AUGUST 21, 1902.

Carter, Wm. H., Water Bureau, Dept. of Public Works, Pittsburg, Pa.
Mueller, Edward, Roanoke, Va.
Watkins, Edwin D., Lafayette Coll., Easton, Pa.

ASSOCIATE ELECTED AUGUST 21, 1902.

Outwater, Raymond, 1312 B. St., S. W., Washington, D. C.

CHANGES OF ADDRESS.

Arsem, Wm. C., 229 Liberty St., Schenectady, N. Y.
Batchelder, Gilbert N., Box 241, Oxnard, Cal.
Blanchard, Arthur A., Newton Centre, Mass.
Davis, R. S., P. R. R. Lab., Altoona, Pa.
Fulweiler, W. H., 1219 Garfield Ave., Kansas City, Mo.
Gifford, Wm. E., 59 Emmett St., Newark, N. J.
Graham, J. Howard, Spanish American Iron Co., Daiquiri, Cuba.
Jackson, Daniel D., 941 President St., Brooklyn, N. Y.
Johnson, E. S., Solvay Process Co., Syracuse, N. Y.
Keller, A. Cornelius, Apartado 68, Aguascalientes, Mexico.
Laist, Frederick, Chem. Dept., Univ. of Utah, Salt Lake City, Utah.
Mackay, Philip A., Cockle Creek, New South Wales, Australia.
Mathews, John A., Crucible Steel Co. of America, Syracuse, N. Y.
Page, R. W., 527 Third St., Brooklyn, N. Y.
Parker, Charles E., 164 New St., New Brunswick, N. J.
Parmelee, H. C., 553 Emerson St., Denver, Colo.
Peter, Alfred M., 268 E. Maxwell St., Lexington, Ky.
Rapalje, E. H., Cronley, N. C.
Rounds, M. B. C., 12024 Stewart Ave., West Pullman, Chicago, Ill.

Rust, Robert R., Beaumont, Texas.
Taylor, H. W., Baker P. O., La.
Thayer, Harry S., Greeley, Colo.
Volckening, G. J., 660 Greene Ave., Brooklyn, N. Y.
Watters, L. L., 142 W. 94th St., N. Y. City.

DECEASED MEMBERS.

Dr. George Mann Richardson, of Stanford University, Cal., member of the Society since 1895, died July 26, 1902.

ADDRESSES WANTED.

Boroschek, L., formerly of 149 E. 56th St., N. Y. City.
Sloane, T. O'Conor, formerly of 35 Broadway, N. Y. City.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

Since November, 1901, the following meetings of the Cincinnati Section have been held and the following papers read:

87th meeting, December 14th (annual meeting): "The Influence of Salts on the Miscibility of Liquids," by J. F. Snell.

88th meeting, January 15th: "On the Relation of the Heat of Combustion to the Specific Gravity of Fatty Oils," by H. C. Sherman and J. F. Snell; "On the Determination of Essential Oils," by L. L. Watters.

89th meeting, February 12th: "Some Curious Mineral and Geological Specimens from Kentucky," by John Uri Lloyd.

90th meeting, March 12th: "Derivatives of Tetrahydroquinoline," by Thomas Evans; "Sulphur in Cottonseed," by T. D. Wetterstroem; "Remarks on Infectious Diseases," by Alfred Springer.

91st meeting, April 16th: "Magnesium Amalgam as a Reducing Agent," by H. S. Fry; "Report on Knietsch's Paper on the Manufacture of Sulphuric Acid by the Contact Process," by J. F. Snell.

92nd meeting, May 19th: "Systems of Water Purification," by J. W. Ellms; "Review of Grignard's Paper on Magnesium Organic Compounds," by Thomas Evans.

93rd meeting, June 9th: "On Adulteration of Lavender Oil with Salicylic Acid," by Everhard Weber; "Meta- and Ana-Bromtetrahydroquinoline," by Geoffrey A. Gray; "A By-prod-

uct of the Alkaline Bromination of Cinnamic Acid," by Lloyd A. Meader.

At the annual meeting the following officers were elected: *President*—R. W. Hochstetter; *Vice-Presidents*—Otto Dieckmann and H. F. Newman; *Secretary*—L. L. Watters; *Treasurer*—B. M. Pilhashy; *Executive Committee*—H. M. Gordin, W. Simonson, and J. F. Snell; *Representative in the Council*—Thomas Evans.

At the June meeting, Dr. Watters resigned the secretaryship, and Dr. J. F. Snell was elected to fill the unexpired term.

J. F. SNELL, *Secretary.*

Issued with October Number, 1902

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Acker, Chas. E., Niagara Falls, N. Y.
Arbuckle, H. B., Agnes Scott Inst., Decatur, Ga.
Bolling, George E., 1257 Belmont St., Brockton, Mass.
Carr, George R., 416 Home Ave., Oak Park, Ill.
Corwin, C. E., 508 5th St., Marietta, O.
Edgar, William H., 27–34 Rialto Bldg., Chicago, Ill.
Fenner, L. M., Watertown, N. Y.
Gerber, Harry, Fremont, Mich.
Grimwood, Charles P., 214 Pine Street, San Francisco, Cal.
Horn, David W., Bryn Mawr, Pa.
Kahn, Julius, Bloomfield, N. J.
Keran, J. N., Fowler, Fresno Co., Cal.
Lyon, D. A., 320 Sansome St., San Francisco, Cal.
Merriam, Edmund S., 314 Collins St., Hartford, Conn.
Muckenfuss, A. M., Univ. of Ark., Fayetteville, Ark.
O'Connell, C. J., Mountain Iron, Minn.
Rose, Lewis H., Univ. of Ark., Fayetteville, Ark.
Ross, Samuel H., 53 Morris, Univ. of Pa. Dormitories, Phila.
Swain, Robert E., Stanford University, Cal.
Trebing, H., Charlotte, Monroe Co., N. Y.
Williams, Frank M., Clarkson School of Technology, Potsdam, N. Y.
Worrell, Steve H., Univ. of Tex., Austin, Texas.

NEW MEMBERS ELECTED SEPTEMBER 26, 1902.

Allen, Wm. P., N. J. Agr. Exp. Station, New Brunswick, N. J.
Fairlie, Andrew M., Detroit Copper and Brass Rolling Mills, Detroit, Mich.
Gray, John H., Jr., 1523 Pt. Lobos Ave., San Francisco, Cal.
Haehnlen, J. L., Otto, Allegheny Co., Pa.
Parrett, Ben. C., Lake Superior Power Co., Sault Ste. Marie, Ont.
Teeple, John E., Cornell Univ., Ithaca, N. Y.
Wheeler, (Miss) May, 802 Oakland Ave., Ann Arbor, Mich.
Woods, Fred L., 418 South St., Iola, Kans.

ASSOCIATE ELECTED SEPTEMBER 26, 1902.

Welch, Charles C., Jr., 1450 Washington Ave., Denver, Colo.

CHANGES OF ADDRESS.

Abbott, Francis L., care of Cia. Fundidora de Fierro y Acero de Monterey, Monterey, Mexico.
Alway, F. J., Nebr. Wes. Univ., University Place, Nebr.
Barrett, Jesse M., R. R. No. 5, Greenfield, Ind.
Beans, H. T., 324 W. 115th St., N. Y. City.
Beistle, Charles P., Frankford Arsenal, Philadelphia, Pa.
Bernhard, Adolph, Stone Creek, Ohio.
Bizzell, J. A., 217 Mitchell St., Ithaca, N. Y.
Bloom, W. E., 312 Ninth St., Sunbury, Pa.
Boesch, B. W., 11 Warren St., Peabody, Mass.
Braman, Winfred W., 129 West St., Worcester, Mass.
Burck, C. A., 418 South St., Iola, Kans.
Clark, Friend E., W. Va. Univ., Morgantown, W. Va.
Comey, Arthur M., 12 Pearl St., Boston, Mass.
Corse, W. M., 258 Horton Ave., Detroit, Mich.
Craig, A. G., Chappaqua, Mountain Inst., Chappaqua, N. Y.
Dains, F. B., Washburn Coll., Topeka, Kans.
Daniel, F. C., 140 R. St., N. E., Washington, D. C.
Desper, E. W., 6 Green Lane, Worcester, Mass.
Devlin, J. A., 315 S. Walnut St., Iola, Kans.
Dunn, W. A., 940 S. Figueroa St., Los Angeles, Cal.
Eccles, David C., Northwestern Univ. School of Pharmacy, Lake and Dearborn Sts., Chicago, Ill.
Exner, Franz F., 110 N. Wanamaker St., Philadelphia, Pa.
Fowler, R. E., 58 Cornell Heights, Ithaca, N. Y.
Fuller, George W., 170 Broadway, N. Y. City.
Godley, Geo. McM., care of Warren Foundry and Machine Co., 160 Broadway, N. Y. City.
Goodell, George A., 529 W. 123rd St., N. Y. City.
Hall, C. A., 517 North American Bldg., Philadelphia, Pa.
Hanzlik, Vaclav, Box 96, Wallaceburg, Ont.
Herms, Edward, care Commonwealth Steel Co., Granite City, Ill.
Hoffman, P. C., Box 562, Montgomery, Ala.
Holbrook, G. M., 6406 Star Ave., Jackson Park, Chicago, Ill.
Hooper, Everett, Warren Chambers, Boston, Mass.
Howard, Henry, Boulevard Sta., Boston, Mass.
Laudig, O. O., Supt. Blast Furnaces, Illinois Steel Co., South Chicago, Ill.
Lee, John C., Boulevard Sta., Boston, Mass.
Lee, Waldemar, Palmerton, Carbon Co., Pa.
Loeb, Morris, Seabright, N. J.
Long, J. H., Lake and Dearborn Sts., Chicago, Ill.
Mabery, C. F., 788 Fairmount St., Cleveland, Ohio.

Marsh, Harry B., 66 Windham St., Willimantic, Conn.
McMurtrie, Wm., 444 West End Ave., New York City.
Montgomery, Jack P., Agricultural College, Miss.
Montgomery, T. S., Oglesby, Ill.
Nelson, E. K., care of Swift & Co. Chem. Lab., U. S. Yards, Chicago, Ill.
Palmer, Charles S., State School of Mines, Golden, Col.
Patterson, Charles W., Lake and Dearborn Sts., Chicago, Ill.
Pemberton, Henry, Jr., 1008 Clinton St., Philadelphia, Pa.
Perkins, T. S., Union Sugar Co., Betteravia, Cal.
Pierson, W. C., 62 Woodward Ave., Atlanta, Ga.
Plank, W. F., care of United Coke & Gas Co., Otto, Allegheny Co., Pa.
Pratt, Joseph H., 141 Broadway, New York City.
Riederer, E. J., 251 W. 95th St., New York City.
Rising, W. B., Univ. of Cal., Berkeley, Cal.
Safford, E. B., 493 42nd Pl., Chicago, Ill.
Schlundt, Herman, Columbia, Mo.
Sloane, T. O'Conor, 35 Wall St., New York City.
Smith, H. E., Chemist L. S. & M. S. Ry., Collinwood, O.
Snelling, W. O., 1313 New York Ave., N. W., Washington, D. C.
Strahorn, A. T., Bureau of Soils, Dept. of Agr., Washington, D. C.
Sullivan, Eugene C., 502 Forest Ave., Ann Arbor, Mich.
Swan, Clifford M., Boulevard Sta., Boston, Mass.
Thompson, Firman, New Carlisle, O.
Wallace, E. C., Cambridgeport, Mass.
Watson, C. A., Salem, N. C.
Watson, E. T., Lock Box 807, Charleston, Kanawha Co., W. Virginia.
Weller, H. R., Univ. of N. C., Chapel Hill, N. C.
Wilkins, A. D., Bellevue P. O. Sta., Allegheny, Pa.
Youtz, L. A., 672 Lawe St., Appleton, Wis.

ADDRESSES WANTED.

Hayes-Campbell, J., formerly of 23 Branch St., St. Louis, Mo.
Kamerer, A. L., formerly of Dormitories Univ. of Pa., Phila., Pa.

DECEASED MEMBER.

Dr. W. M. Mew, of Washington, D. C., member of the Society since 1892, died Sept. 19, 1902. Dr. Mew had been for thirty years in the medical department of the army, and was a member of the U. S. Pharmacopoeial Revision Committee.

MEETINGS OF THE SECTIONS.

PHILADELPHIA SECTION.

The annual meeting of the Section was held May 12th. The following officers were elected: *President*—Henry Leffmann; *Secretary* and *Treasurer*—F. E. Dodge; *Exec. Com.*—Jesse Jones, George E. Thomas, L. F. Kebler. The retiring chairman, J. Merritt Matthews, gave an address on "Some Phases of Textile Chemistry," and the paper was discussed by Messrs. Withrow, Leffmann, Sabin, and Taggart.

On June 12th, the following papers were presented: "The Relation of Chemistry to the National Government," illustrated by lantern slides, by H. W. Wiley; "The Steel Works Laboratory," by George W. Sargent; "Carbon by Combustion," by George Auchy.

F. E. DODGE, *Sec'y.*

KANSAS CITY SECTION.

Since the beginning of the year 1902 the Kansas City Section has held the following meetings:

10th meeting, January 14: "The Manufacture and Chemistry of Portland Cement," by E. C. Champion.

11th meeting, February 11th: "The Manufacture and Chemistry of Fertilizers," by Jesse M. Barrett.

12th meeting, March 11th: "Some Alkaloids and their Synthetical Preparation" and "Some Derivatives of Quinoline Prepared at Kansas University," by Edward Bartow.

13th meeting, April 22nd: "Liquid Air," by E. C. Franklin; this lecture was illustrated by experiments, being delivered at the University of Kansas, where Professor Franklin has an air-liquefying plant.

14th meeting, May 20th: "Colloidal Solutions," by Lucien I. Blake.

ARMAND R. MILLER, *Sec'y.*

Issued with November Number, 1902.

Proceedings.

COUNCIL.

DEAR SIR:

Article XII of the Constitution of the American Chemical Society provides that "the assent of two-thirds of the members voting on an amendment shall be necessary to its adoption." It will be seen from the following report of the canvassers that each one of the amendments recently submitted to the Society has been adopted:

BROOKLYN, N. Y., October 23, 1902.

We, the undersigned, hereby certify that the following is the result of the canvass of ballots received from members of the American Chemical Society, upon the proposed amendments to the Constitution of the Society, submitted September 16, 1902:

In favor of amendment one	360
Against amendment one	86
In favor of amendment two	360
Against amendment two	68
In favor of amendment three	372
Against amendment three	68
In favor of amendment four	395
Against amendment four	45
In favor of amendment five	391
Against amendment five	42

ALBERT C. HALE,
W. H. BROADHURST,
W. CASAMAJOR,
Canvassers.

The paragraphs of the constitution, designated below, are therefore amended to read as follows:

Article III, Section 1.—"The Society shall consist of members, life members, and honorary members."

Article III, Section 2.—"Any person interested in the promotion of chemistry may be nominated for election as a member."

Article III, Section 3.—"Any person who shall have been nominated in writing in due form by three members of the Society, and whose nomination shall have been endorsed by a majority of the Committee on Membership, shall be declared elected a member of the Society, which declaration shall be made public by the secretary on receipt of said endorsement."

Article III, Section 4.—"Any member, not in arrears, paying at any one time the sum of one hundred dollars into the treasury of the Society as commutation for dues, shall become a life member, shall be exempt from the further payment of annual dues, and shall receive all the regular publications of the Society."

Article III, Section 5.—(The former Section 8.)

Article III, Section 6.—(The former Section 9, omitting the words "and honorary associates" in paragraph 2.)

Article VII.—"A Journal, published by the Society, shall be distributed to all members not in arrears."

By-Laws 13, 15, 16, 17, 18.—Omit the words "or associates" and "and associates" wherever occurring.

The Index of the first twenty volumes of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 1879–1898, and of the Proceedings, 1877–1879, is now published. Copies can be ordered from the librarian, Dr. E. G. Love, 108 W. 55th Street, N. Y. City. Rates, 50 cents to members of the Society; 75 cents to non-members.

ALBERT C. HALE, *Secretary.*

NEW MEMBERS ELECTED BETWEEN SEPTEMBER 26 AND OCTOBER 27, 1902.

Acker, Charles E., Niagara Falls, N. Y.

Arbuckle, H. B., Agnes Scott Inst., Decatur, Ga.

Banks, W. G., Elk Rapids, Mich.
Bartsch, Charles A., 6803 Woodland Ave., Philadelphia, Pa.
Baruch, Edgar, 100 California St., San Francisco, Cal.
Baxter, Albert C., 814 W. College Ave., Jacksonville, Ill.
Bolling, George Everett, 1257 Belmont St., Brockton, Mass.
Booth, Wm. M., Cortland, N. Y.
Carr, George R., 416 Home Ave., Oak Park, Ill.
Catlett, George F., Chapel Hill, N. C.
Corwin, C. E., 508 5th St., Marietta, O.
Crane, Jasper E., 20 Central Ave., Newark, N. J.
Edgar, Wm. H., 27–34 Rialto Bldg., Chicago, Ill.
Fenner, L. M., Watertown, N. Y.
Frank, Henry, 378 Vanderbilt Ave., Brooklyn, N. Y.
Gerber, Harry, Fremont, Mich.
Gleason, Gilbert H., 12 Ruthven St., Roxbury, Mass.
Grimwood, Charles P., 214 Pine St., San Francisco, Cal.
Higgins, Francis W., 549 4th St., Niagara Falls, N. Y.
Horn, David W., Bryn Mawr, Pa.
Hughes, Louis S., 4 Burton Pl., Chicago, Ill.
Keran, J. N., Fowler, Fresno Co., Cal.
Landis, Walter S., 48 Church St., Bethlehem, Pa.
Lyon, D. A., 320 Sansome St., San Francisco, Cal.
Mahin, Edward G., 141 Pierce St., W. Lafayette, Ind.
Merriam, Edmund S., 314 Collins St., Hartford, Conn.
Miller, Robert, Lucy Furnaces, 51st St., Pittsburg, Pa.
Muckenfuss, A. M., Univ. of Arkansas, Fayetteville, Ark.
Newburg, Mervyn J., 1954 Bush St., San Francisco, Cal.
O'Connell, C. J., Mountain Iron, Minn.
Peck, C. F., 213 MacDougall Ave., Detroit, Mich.
Powell, James, Spring Grove Ave., Cincinnati, O.
Rose, Lewis H., Univ. of Arkansas, Fayetteville, Ark.
Ross, Samuel H., 53 Morris, Univ. of Pa. Dormitories, Philadelphia, Pa.
Sohler, Frank E., Palo Alto, Cal.
Swain, Robert E., Stanford University, Cal.
Taylor, Alonzo E., 1809 Broadway, San Francisco, Cal.
Trebing, H., Charlotte, N. Y.
Turner, Harold J., 1720 N. 15th St., Philadelphia, Pa.
Williams, Frank M., Clarkson School of Tech., Potsdam, N. Y.

Worrell, Steve H., Univ. of Texas, Austin, Texas.

CHANGES OF ADDRESS.

Annear, J. B., Livingston Mill, Sugar Loaf, Colo.

Baldwin, W. S., Platten Str. 50, Pension Englebrecht, Zürich, Switzerland.

Baringer, F. J., care of Eagle White Lead Co., 1020 Broadway, Cincinnati, O.

Bird, Maurice, Asheville, N. C.

Breed, Miss Mary B., East 3rd St., Bloomington, Ind.

Cary, Edward A., 66 Clinton Ave., Montclair, N. J.

Case, Wm. A., 345 Campbell Ave., S. W., Roanoke, Va.

Clevenger, G. H., 432 W. 124th St., N. Y. City.

Closson, C. D., 331 N. Union St., Fostoria, O.

Doerflinger, Wm. F., 113 Chelton Ave., Niagara Falls, N. Y.

Downey, James E., 14 Kendall St., Worcester, Mass.

Gordon, F. T., U. S. R. S. "Wabash," Navy Yard, Boston, Mass.

Gross, John, Penobscot Mining Co., Deadwood, S. D.

Haas, Herbert, Apt. 116, Torreon, Coahuila, Mexico.

Hall, R. D., 3465 Sansom St., Philadelphia, Pa.

Hand, W. F., Agricultural College, Miss.

Hargrove, Julian O., 1603 O St., N. W., Washington, D. C.

Hemmings, Fred J., Room 520, Weld Bldg., 176 Federal St., Boston, Mass.

Henwood, Abraham, 1802 Chestnut St., Philadelphia, Pa.

Hewitt, E. R., Tuxedo Park, N. Y.

Hibbard, P. L., 2291 N. 41st Court, Chicago, Ill.

Hopkins, Erastus, Lake Helen, Florida.

Jackson, D. D., Mt. Prospect Lab., Flatbush Ave., and Eastern Parkway, Brooklyn, N. Y.

Jefferson, Miss A. M., 165 Hansberry St., Germantown, Philadelphia, Pa.

Kingman, W. A., 164 Central St., Leominster, Mass.

Koelle, Carl, care of Amer. S. and R. Co., 71 Broadway, N. Y. City.

Kohr, D. A., Bond Hill, Hamilton Co., Ohio.

Loeb, Morris, 37 E. 38th St., N. Y. City.

Long, J. H., 2421 Dearborn St., Chicago, Ill.

Ludlow, S. H., care of Nat. Portland Cement Co., Durham, Ontario.

May, George A., "The Fabrikoid Co.," Newburgh, Orange Co., N. Y.

McCullough, J. E., 327 W. Pittsburgh St., Greensburg, Pa.

Miyaké, H., No. 46 Naka no cho, Okayama, Japan.

Myers, Ralph E., John Harrison Lab. of Chem., Univ. of Pa., Philadelphia, Pa.

Nelson, E. K., Paris, Ill.

Overton, A. G., care of Steel Plant Laby., Ensley, Ala.

Page, Robert W., 510 Twelfth St., Brooklyn, N. Y.

Porter, A. F., Haskell, N. J.

Porter, Fred B., 4811 Evans Ave., Chicago, Ill.

Pilhashy, B. M., 1325 Lincoln Ave., Walnut Hills, Cincinnati, O.

Prohaska, O. L., 634 N. Rockwell St., Chicago, Ill.

Ritchey, J. C., 1897 Superior St., Cleveland, O.

Roberts, Alfred E., 1949 7th Ave., N. Y. City.

Rogers, Allen, 4627 Paschall Ave., Philadelphia, Pa.

Rounds, M. B. C., Leaf River, Ill.

Safford, E. B., care of Nelson Morris and Co., U. S. Yards, Chicago, Ill.

Sanders, Warren W., Victor Chem. Wks., Chicago Heights, Ill.

Simmons, Ward W., 80 St. Nicholas Ave., N. Y. City.

Starke, Eric A., 1024 Union St., Alameda, Cal.

Steiger, George, U. S. Geol. Survey, Washington, D. C.

Stocker, J. H., 488 Nostrand Ave., Brooklyn, N. Y.

Thayer, Harry S., 526 West 114th St., N. Y. City.

Tibbals, Chas. Austen, Jr., Univ. of Wis., Madison, Wis.

Tingle, Alfred, 41 Alexander St., Toronto, Ontario.

Topping, A. N., 1035 Barnett Ave., Kansas City, Kans.

Wakeman, A. J., Green Farms, Conn.

Webb, E. H., Trenton Iron Wks., Trenton, N. J.

Williams, Robert S., Mass. Inst. Tech., Boston, Mass.

ADDRESSES WANTED.

Hopkins, Matthew S., formerly of "The Roylston," Baltimore, Md.

Myers, R. G., formerly of 819 Willson Ave., Cleveland, Ohio.

Odell, J. R., formerly of 157 Huntington Ave., Boston, Mass.

Reid, Burton, formerly of Central High School, Kansas City, Mo.

CHICAGO SECTION.

The October meeting of the Chicago Section was held on the evening of the 21st at the Hotel Bismark. A table-de-hôte dinner was served at 6.30, and following this a very interesting paper was given: "What the Chemist Can Do to Conserve Public Health," by Dr. H. W. Wiley of the U. S. Bureau of Agriculture.

W. A. CONVERSE, *Sec'y.*

Issued with December Number, 1902.

Proceedings.

FIFTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

The Fifth International Congress of Applied Chemistry will begin its sessions in Berlin, on May 31, 1903.

The permanent Committee on Organization, holding over from the meeting of the Fourth Congress, in Paris, has designated Professor Clemens Winkler as President of Honor and Professor Otto N. Witt as President of the German Committee.

At the request of this committee and in accordance with the resolution passed by the Council of the American Chemical Society, the president of the Society has appointed the following American Committee on Organization:

H. W. Wiley, Chairman, Chief of Bureau of Chemistry, Department of Agriculture, Washington, D. C.

Section I.—Analytical Chemistry, Apparatus, and Instruments: Dr. W. F. Hillebrand, Chemist, U. S. Geological Survey, Washington, D. C.; O. P. Amend, Secretary of the firm of Eimer & Amend, 205 Third Avenue, New York, N. Y.; Charles Baskerville, Ph.D., F.C.S., Smith Professor of General Chemistry and Director of the Laboratory, University of North Carolina, Chapel Hill, N. C.; E. E. Ewell, Assistant Chief of Bureau of Chemistry, Department of Agriculture, Washington, D. C.; William A. Noyes, Professor of Chemistry, Rose Polytechnic Institute, Terre Haute, Ind.

Section II.—Chemical Industries of Inorganic Products: Dr. Edward Hart, Professor of Chemistry, Lafayette College, Easton, Pa.; J. D. Pennock, Chief Chemist, Solvay Process Co. and Semet-Solvay Co., Syracuse, N. Y.; Geo. C. Stone, Chief Engineer, New Jersey Zinc Co., 11 Broadway, New York, N. Y.; Frederic J. Falding, of Exchange Court, 52 Broadway, New York, N. Y.

Section III.—Metallurgy, Mining, and Explosives: Charles E. Munroe, Ph.D., Professor of Chemistry, The Columbian University, Washington, D. C.; A. E. Knorr, Chief Chemist, Baltimore Copper Smelting and Rolling Co., Canton, Baltimore, Md.;

Francis C. Phillips, Professor of Chemistry, Western University, Allegheny, Pa.; W. B. Rising, Professor of Chemistry, University of California, Berkeley, Cal.

Section IV.—Chemical Industries of Organic Products: (*a*) Organic Preparations, including coal-tar products; (*b*) Dyestuffs and their uses: William McMurtrie, Consulting Chemist, Royal Baking Powder Co., New York, N. Y.; J. Merritt Matthews, Ph.D., Professor in charge of Chemical Dyeing Dept., Philadelphia Textile School, Philadelphia, Pa.; Clifford Richardson, Director of the New York Testing Laboratory, Long Island City, N. Y.; Samuel P. Sadtler, Ph.D., LL.D., Consulting Chemist and Honorary Professor of Chemistry, Franklin Inst. of Philadelphia, 10th and Chestnut Sts., Philadelphia, Pa.

Section V.—Sugar Industry: Dr. F. G. Wiechmann, Consulting Chemist, American Sugar Refining Co., Box 79, Station W, Brooklyn, N. Y.; Arno Behr, Ph.D., Chemist, Pasadena, Cal.; David L. Davoll, Jr., Chief Chemist, Peninsular Sugar Refining Co., Caro, Mich.; W. D. Horne, Ph.D., Consulting Chemist, The National Sugar Refining Co. of New Jersey, Yonkers, N. Y; G. L. Spencer, Chief of Sugar Laboratory, Bureau of Chemistry, Dept. of Agriculture, Washington, D. C.

Section VI.—Fermentation and Starch Manufacture: Max Henius, Ph.D., Director, American Brewing Academy and the Scientific Station for Brewing, Chicago, Ill.; Charles E. Pellew, E.M., Adjunct Professor of Chemistry, Columbia University, New York, N. Y.; Alfred Springer, Ph.D., Chemist, 312 E. 2d St., Cincinnati, O.

Section VII.—Agricultural Chemistry: B. W. Kilgore, Director, North Carolina Agricultural Experiment Station and State Chemist, Raleigh, N. C.; Henry Adam Weber, Ph.D., Professor of Agricultural Chemistry, Ohio State University, Columbus, O.; Chas. D. Woods, Professor of Agriculture, University of Maine, and Director of Maine Agricultural Experiment Station, Orono, Maine; B. B. Ross, Professor of Chemistry, Alabama Polytechnic Institute and State Chemist of Alabama, Auburn, Ala.

Section VIII.—Hygiene, Chemical and Pharmaceutical Chemistry: Foods; M. E. Jaffa, Assistant Professor of Chemistry, University of California, Berkeley, Cal.; W. O. Atwater, Professor of Chemistry, Wesleyan University, Middletown, Conn., Chief of Nutrition Investigation, Office of Experiment Stations, U. S. Department of Agriculture; E. A. de Schweinitz, Chief Biochemic Division, Department of Agriculture, Dean and Professor of Chemistry, Columbian University Medical School, Washington, D. C.; Walter S. Haines, Professor of Chemistry, Pharmacy and Toxicology, Rush Medical College, Chicago, Ill.; Edward Kremers, Professor of Pharmaceutical Chemistry, Di-

rector of School of Pharmacy, University of Wisconsin, Madison, Wis.; John Marshall, Professor of Chemistry and Toxicology, University of Pennsylvania, Philadelphia, Pa.; John Uri Lloyd, Ph.D., LL.D., Professor of Chemistry, Eclectic Medical Institution, Cincinnati, O.; W. P. Mason, Professor of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y.

Section IX.—Photochemistry: Dr. L. H. Friedburg, late Professor of Chemistry and Toxicology at the Flower Hospital Medical College, New York; Address, 529 West 147th St., New York, N. Y.; Dr. Peter T. Austen, F.C.S., Chemical Expert, 80 Broad St., New York, N. Y.; Leo Baekeland, D.Sc., Research Chemist, 'Snug Rock,' N. Broadway (Harmony Park), Yonkers, N. Y.

Section X.—Electrochemical and Physical Chemistry: Charles A. Doremus, M.D., Ph.D., Assistant Professor of Chemistry, College of the City of New York, N. Y.; W. D. Bancroft, Assistant Professor of Physical Chemistry, Cornell University, Ithaca, N. Y.; Edgar F. Smith, Professor of Chemistry, University of Pennsylvania, Philadelphia, Pa.; C. F. Chandler, Professor of Chemistry, Columbia University, New York, N. Y.; A. A. Noyes, Professor of Theoretical and Organic Chemistry, Massachusetts Institute of Technology, Boston, Mass.

Section XI.—Legal and Agricultural Problems in connection with the Chemical Industries: Dr. J. W. Mallet, Professor of Chemistry, University of Virginia, Charlottesville, Va.; Charles B. Dudley, Chief Chemist, Pennsylvania R. R. Co., Altoona, Pa.; Albert B. Prescott, Director of Chemical Laboratory, University of Michigan, Ann Arbor, Mich.; S. P. Sharples, Analytical and Consulting Chemist, 13 Broad St., Boston, Mass.; A. H. Todd, Manufacturing Chemist and Distiller of Essential Oils, Kalamazoo, Mich.

A few other gentlemen have been appointed on the committee, but their acceptances have not yet been received. It is hoped that American chemists will become members of this Fifth Congress in large numbers, even if they are not able to be present in person, and that as many as possible will attend. Both those who can attend and those who are not able to go are urged to send papers.

The work of the Congress has been organized in the sections given above. The members of the committee in each section should endeavor particularly to promote the interest of that branch of the science which specially belongs to that section.

The fee for membership is 20 marks or $4.76. To avoid the trouble of sending separate postal orders for this sum the chair-

man of the committee, Dr. Wiley, will undertake to transmit to Berlin the membership fees of American chemists who wish to avail themselves of this opportunity. Those desiring, therefore, to become members may send their personal check for $4.76 and nine cents to cover postage, postal order, etc., in all $4.85, to Dr. H. W. Wiley, Chief of the Bureau of Chemistry, Department of Agriculture, Washington, D. C., who will give them a receipt for the same while waiting for an official receipt from the treasurer at Berlin.

If reductions in steamship rates can be obtained, a notice to the effect will be published in *Science* and the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY. Members attending the Congress should leave the United States not later than the 15th of May by slow steamer, nor the 20th of May by fast steamer.

The official announcements and other circular matter connected with the Congress will be distributed through the American committee as soon as the documents are received from Berlin. Any members of the Society to whom these circulars may not be sent can secure them by writing to the chairman of the American Committee.

Chemists not members of the American Chemical Society are also cordially invited to participate in the Congress both as members and as authors of papers and the same courtesies will be extended to them, if so desired, as are offered above.

H. W. WILEY.

Member of Permanent Committee on Organization and Chairman of American Committee.

BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held in the library of the Chemists' Club, 108 W. 55th Street, N. Y. City, Friday, October 10, 1902. The directors present were Messrs. Doremus, Hale, Hallock, and Smith.

The meeting was called to order by the secretary at 8.30 P.M., and in the absence of the president, Professor C. A. Doremus was chosen chairman *pro tem.*

The minutes of the previous meetings of the directors were approved as recorded by the secretary.

The librarian was authorized to sell to the *Deutsche Chemische*

Gesellschaft at the rate of $4.00 per volume such volumes of the Journal as that society might wish to purchase in connection with the making of arrangements for an exchange of the *Berichte* for the Journal of the American Chemical Society.

The librarian was also authorized and directed to take charge of the sale of the Index of the first twenty volumes of the Journal and the Proceedings of the Society at the prices already fixed by the directors, namely, fifty cents per copy to members of the Society, and seventy-five cents per copy to non-members.

The secretary was directed to transfer to the librarian all property of the Society remaining in his hands at the close of his term of office, and which shall not be needed by his successor.

The meeting of the directors was then adjourned.

ALBERT C. HALE, *Secretary.*

COUNCIL.

The Council has approved the following resolution: "It is hereby ordered that in the event of the passage of the amendments now pending, all persons who at that time shall be on the roll of the Society as Associates or Life Associates shall thereupon become Members or Life Members, respectively, of the Society."

The amendments having all been passed, all Associates and Life Associates are hereby declared Members and Life Members, respectively.

In response to an invitation from the Managers and Faculty of Swarthmore College, President Remsen appointed Professor Edgar F. Smith, of the University of Pennsylvania, to represent the American Chemical Society at the inauguration of Joseph Swain, LL.D., as President of Swarthmore College, on the morning of November 15, 1902.

MEMBERS ELECTED BETWEEN OCTOBER 28 AND NOVEMBER 27, 1902.

Abraham, Herbert, 13 W. 89th St., N. Y. City.
Andrews, (Miss) Catherine E., 1095 N. High St., Columbus, O.
Bahlmann, Clarence, 3201 Woodburn Ave., Cincinnati, O.
Beardslee, R. P., 13 South St., Ithaca, N. Y.
Bennett, Hugh H., Chapel Hill, N. C.
Bleininger, Albert V., 116 W. 9th Ave., Columbus, O.
Brooke, John C., Bureau of Soils, Dept. of Agr., Washington, D. C.

Brooks, H. Kibbee, Bellows Falls, Vt.
Browne, Arthur W., 217 Mitchell St., Ithaca, N. Y.
Burrows, George H., 221 Eddy St., Ithaca, N. Y.
Carlton, Henry A., 33 Holyoke St., Cambridge, Mass.
Cavanaugh, George W., Cornell Univ. Agr. Expt. Sta., Ithaca, N. Y.
Clark, W. Blair, Granville, O.
Coover, Winfred F., 1456 Hunter St., Columbus, O.
Drake, Bryant S., care of Peyton Chemical Co., Martinez, Cal.
Dubois, Wilbur L., 1213 Q St., Washington, D. C.
Eastwood, John F., 713 E. Huron St., Ann Arbor, Mich.
Fuller, Robert W., 174 W. 102nd St., N. Y. City.
Garrard, James G., care of Crane Co., 52 Judd St., Chicago, Ill.
Gilpin, J. Elliott, Johns Hopkins Univ., Baltimore, Md.
Greenwood, Ernest H., 15 South Ave., Ithaca, N. Y.
Haigh, Leonard D., 713 E. Catharine St., Ann Arbor, Mich.
Hawley, Lee F., 113 Osmun Place, Ithaca, N. Y.
Heike, Rudolph E., Box 722, N. Y. City.
Henning, C. J., Cal. Powder Works, Santa Cruz, Cal.
Hirsch, Rudolph, 1060 S. Front St., Columbus, O.
Hopkins, Henry S., Bainbridge, N. Y.
Isham, (Miss) Helen, 3 Central Ave., Ithaca, N. Y.
Jessel, Henry R., 1 Cascadilla Place, Ithaca, N. Y.
Johnson, Charles W., 215 Glenn Ave., Ann Arbor, Mich.
Johnston, O. P., 123 Linn St., Ithaca, N. Y.
Karas, John I., care Central Star Laundry, Northland Ave., Buffalo, N. Y.
Kern, Wm. F., 75 W. 10th Ave., Columbus, O.
Kluttz, Warren, care of Tenn. C. I. & R. Co., Bessemer, Ala.
Kortright, Frederic L., Morgantown, W. Va.
Lichty, David M., 922 Olivia Ave., Ann Arbor, Mich.
Loudon, Archd. M., 544 W. 126th St., New York City.
Lundell, Gustavous E. F., 115 Mitchell St., Ithaca, N. Y.
MacLeod, (Miss) Grace, Mount Hermon School, Mount Hermon, Mass.
Mandel, John A., 338 E. 26th St., N. Y. City.
Marckworth, O. S., 250 Wilbur Ave., Columbus, O.
Masury, Frederick L. M., 43 W. 87th St., N. Y. City.
Mayer, Andrew, Jr., 104 St. Marks Ave., Brooklyn, N. Y.
Middleton, Arthur A., 115 Cook St., Ithaca, N. Y.
Monroe, Joseph E., Dillon, Mont.
Mowat, J. F., 316 Heustis St., Ithaca, N. Y.
Mueller, Max E., 523 E. Madison St., Ann Arbor, Mich.
Mumma, Marion W., 47 W. 11th Ave., Columbus, O.
Ohler, Wm. H., 18 Locust St., Portland, Me.
Oldham, E. W., 1725 Oregon Ave., St. Louis, Mo.
Orndorff, Wm. R., Cornell Univ., Ithaca, N. Y.

Osborn, Abner A., 197 N. Washington Ave., Columbus, O.
Parker, J. Heber, 115 Cook St., Ithaca, N. Y.
Pumpelly, Laurence, 415 Stewart Ave., Ithaca, N. Y.
Robb, John W., 17 South Ave., Ithaca, N. Y.
Robinson, F. C., 222 Eddy St., Ithaca, N. Y.
Rueger, Charles E., Box 152, Butte, Mont.
Russell, Joseph H., 309 Eddy St., Ithaca, N. Y.
Schade, James W., 266 Hooper St., Brooklyn, N. Y.
Setzler, Horace B., Hotel Sabine, Port Arthur, Texas.
Smeaton, Wm. G., 529 Walnut St., Ann Arbor, Mich.
Smith, Morgan B., 115 Cook St., Ithaca, N. Y.
Snowdon, Ralph C., 205 Hazen St., Ithaca, N. Y.
Stewart, Andrew, 1420 Q St., N. W., Washington, D. C.
Sweeton, (Miss) Agnes G., Sage Hall, Cornell Univ., Ithaca, N. Y.
Taylor, Benjamin F., Gainesville, Ga.
Tefft, Henry D., 111 Quarry St., Ithaca, N. Y.
Terrell, Arthur D., Iola, Kansas.
Thompson, John F., 21 First Place, Brooklyn, N. Y.
Trevor, J. E., 125½ Quarry St., Ithaca, N. Y.
Troy, Hugh C., Cornell Univ., Ithaca, N. Y.
Urner, Frank A., 221 Eddy St., Ithaca, N. Y.
Watling, W. Lee, Northwestern Fertilizing Co., Chicago, Ill.
Weber, Raxley F., 801 E. State St., Ithaca, N. Y.
Williamson, Homer D., W. 10th Ave., Columbus, O.
Witman, Dwight N., 1011 Oak St., Columbus, O.
Wright, Ralph G., 510 Whittier St., St. Louis, Mo.
Young, R. A., 322 Wilbur Ave., Columbus, O.

CHANGES OF ADDRESS.

Anderson, Duncan, Jr., Sydney, Nova Scotia.
Ashley, Harrison E., Box 291, Leetonia, O.
Attix, James C., St. Ignace Furnace, St. Ignace, Mich.
Bolling, Randolph, Allegheny Ore and Iron Co., Victoria Furnace, Goshen, Va.
Bowers, John A., Chester, Pa.
Braman, Winfred W., Lowell Textile School, Lowell, Mass.
Bregowsky, I. M., care of Crane Co., 52 Judd St., Chicago, Ill.
Browne, Chas. A., Jr., Audubon Park, New Orleans, La.
Cameron, Frank K., Bureau of Soils, Dept. of Agr., Washington, D. C.
Clark, Harry A., 189 Harriet St., Bridgeport, Conn.
Danziger, J. L., Columbia Univ., N. Y. City.
Dixon, John B., Brown's Hotel, Glens Falls, N. Y.
Dudley, Charles B., Drawer 156, Altoona, Pa.
Earle, Richard B., Kent Chem. Lab., Univ. of Chicago, Chicago, Ill.

Eldred, Frank R., 1111 N. Illinois St., Indianapolis, Ind.
Fireman, Peter, 206 S St., N. E., Washington, D. C.
Fuller, Frederick D., 84 Lyceum St., Geneva, N. Y.
Goodell, George A., 529 W. 123rd St., New York City.
Gronemeyer, H. H., 315 Amesbury Ave., Cleveland, O.
Gruenberg, Benj. C., 60 W. 13th Street, New York City.
Harris, C. D., 211 William St., Ithaca, N. Y.
Havens, Franke S., 35 Burling Slip, N. Y. City.
Hendee, Edward, University Heights, N. Y. University, N. Y. City.
Hibbard, P. L., 2291 N. 41st Court, Chicago, Ill.
Higgins, Albert W., The National Ammonia Co., St. Louis, Mo.
James, Joseph H., Clemson College, S. C.
Jennings, Fred. H., Orchard Place, Ithaca, N. Y.
Kelly, Wm. E., care of American Magnesia and Covering Co., Plymouth Meeting, Pa.
Kneeland, Fred. R., Mass. Inst. Tech., Boston, Mass.
Law, Leroy M., 613 8th St., N. E., Washington, D. C.
Masson, V. E., Hammondsport, N. Y.
Mende, Alex. P., 120 Liberty St., New York City.
Odell, John R., Technology Chambers, Irvington St., Boston, Mass.
Page, Robt. W., 527 Third St., Brooklyn, N. Y.
Perkins, Albert S., 70 Lyndhurst St., Dorchester, Mass.
Prentiss, George N., 2910 Clybourn St., Milwaukee, Wis.
Remington, J. Percy, 1832 Pine St., Philadelphia, Pa.
Rich, Charles H., Clairton, Pa.
Schuyler, Erwin H. 535 W. 7th St., Erie, Pa.
Simons, Frank D., Div. of Chem., Bureau of Int. Rev., Treas. Dept., Washington, D. C.
Skinner, Hervey J., care Little & Walker, 19 Exchange Pl., Boston, Mass.
Sovereign, C. L., care Glucose Sugar Refining Co., Chicago, Ill.
Stoddart, Charles W., Box 103, Boulder, Colo.
Summey, A. E., Hamburg, N. Y.
Torrey, Joseph, Jr., 108 Beck Ave., Akron, O.
Turner, B. Bernard, 103 Linn St., Ithaca, N. Y.
Van Brunt, Charles, 124 E. 28th St., N. Y. City.
Vannier, Charles H., care of Griffin Wheel Co., Sacramento Square, Chicago, Ill.
Veitch, F. P., Bureau of Chemistry, Washington, D. C.
Volney, C. W., Keyport, N. J.
Von Rücker, Dr. H., care Buchenau and Co., Torreon, Coahuila, Mexico.
Vorce, La Fayette D., 1437 Waller St., Dakotar, Ill.
Washburn, J. H., National Farm School, Doylestown, Pa.

Wiley, Samuel W., American Agricultural Chemical Co., Lazaretto Works, Baltimore, Md.

Wirth, Adam, 920 Delachaise St., New Orleans, La.

ADDRESSES WANTED.

Arsem, Wm. C., formerly of 229 Liberty St., Schenectady, N.Y.

Duryea, Chester B., formerly of "The Earlington," W. 27th St., N. Y. City.

Frank, J. W., formerly of 29 Broadway, N. Y. City.

Titus, (Miss) Winifred, formerly of 425 Park St., Madison, Wis.

MEETINGS OF THE SECTIONS.

NORTH CAROLINA SECTION.

The North Carolina Section held its fall meeting in the office of the State Chemist, Agricultural Building, Raleigh, N. C., on Saturday, November 22, 1902, with Presiding Officer Charles E. Brewer in the chair. Twenty members and visitors were in attendance. Hereafter all papers presented will be required to be in abstract. Drs. A. S. Wheeler and G. S. Fraps were elected reviewers for the section for the ensuing year. Their duties will be for each to prepare and present at some meeting during the year a paper, giving briefly the advances recently made in some branch of chemistry. This departure promises to be a valuable addition to the programs.

The following papers were presented and discussed: "Some New Double Sulphates of Lanthanum, and on the Existence of Lanthanum Alums," by Charles Baskerville and E. G. Moss; "Lanthanates," by Charles Baskerville and G. F. Catlett; "Studies in Nitrification," by G. S. Fraps; "Improved Method for the Determination of Halogens in Atomic Weight Work," by Charles Baskerville and R. O. E. Davis; "Chlorides in Tobacco," by W. H. Pegram; "Suggested Change in the Law of Dulong and Petit," by J. E. Mills; "Neodymates," by Charles Baskerville and W. O. Heard; "Artificial Plant Food Requirements of Soils," by B. W. Kilgore; and "Methods for the Determination of Total Phosphoric Acid and Potash in Soils," by C. B. Williams.

There being no further business, the section adjourned subject to the call of the Executive Committee.

C. B. WILLIAMS, *Secretary.*

NEW YORK SECTION.

The first regular meeting of the New York Section, for the season of 1902–1903, was held October 10th, in the Assembly Hall of the Chemists' Club, 77 members being present.

The following papers were read: Leo Baekeland on "Oxychloride of Magnesium and Its Industrial Uses." The paper was fully illustrated by specimens obtained by combination of magnesia cement with sawdust, asbestos, and other materials.

Dr. H. Schweitzer being unavoidably absent, the descriptive portion of his paper on "Some New Photographic Chemicals" was read by Mr. Bugg, who also exhibited an interesting series of slides, showing the results obtained by the use of the various developers, restrainers, and intensifiers mentioned.

The November meeting was held November 7th, with 53 members present.

The programme was as follows: H. C. Sherman: (1) "The Determination of Sulphur and Phosphorus in Organic Materials." (2) "The Composition of Cows' Milk." F. W. Traphagen and Edmund Burke: "The Occurrence of Salicylic Acid in Fruits." Read by Professor M. T. Bogert.

FRANCIS D. DODGE, *Secretary.*

DECEASED MEMBERS.

Dr. Edwin E. Hunter, of St. Joseph, Mo., member of the Society since 1900, died in the early fall.

Mr. Herbert S. Burgess, of Providence, R. I., associate in the Society, since 1893, died October 15, 1902.

Professor Robert Clark Kedzie, member of the Society since 1894, died November 7, 1902. Professor Kedzie had been professor of chemistry in the Michigan Agricultural College for forty years, and was made professor emeritus last June.

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